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A Literature Review

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FATE AND BIOLOGICAL EFFECTS OF OIL WELL DRILLING FLUIDS IN THE MARINE ENVIRONMENT: A LITERATURE REVIEW

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16. ABSTRACT

The potential impact of drilling fluids on the marine environment is discussed. Prediction of impacts are difficult because no two drilling fluids are identical. They are custom-formulated to perform a variety of functions integral to each drilling operation. Further, drilling fluids are released in a variety of marine systems from artic to temperate seas. Descriptions of the physical and chemical aspects of the plume that results from the release of drilling fluids, as well as a review and discussion of laboratory- and field-derived data on the effects of these fluids on marine organisms, are presented. Laboratory acute toxicity data indicate that lethal and sublethal concentrations of drilling fluids on various marine organisms vary from about 100 parts per million (ppm) in coral to more than 1000 ppm in other less sensitive organisms. Bioaccumlation of heavy metals associated with drilling fluid is discussed. Recommendations are given for preventing or ameliorating drilling-fluid damage to the marine environment. Additional research is proposed to close important gaps in current knowledge about behavior of drilling fluids in aquatic ecosystems.

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FOREWORD

The protection of our estuarine and coastal areas from damage caused by toxic organic pollutants required that regulations restricting the introduction of these compounds into the environment be formulated on a sound scientific basis. Accurate information describing dose-response relationships for organisms and ecosystems under varying conditions is required. The Environmental Research Laboratory, Gulf Breeze, contributes to this information through research programs aimed at determining:

> the effects of toxic organic pollutants on individual species and communities of organisms;
>
> the effects of toxic organics on ecosystem processes and components;
>
> the significance of chemical carcinogens in the estuarine and marine environment.

In recent years, environmental concerns have been voiced that fluids used in offshore oil exploration and production may be acutely toxic or cause deleterious sublethal effects in sensitive aquatic organisms and ecosystems. This report attempts to summarize field and laboratory data published in the scientific literature on the potential impact of compounds found in water-based muds used in oil drilling off the U.S. coast. Additional research is proposed to close important gaps in current knowledge about the impact of drilling fluids in the marine environment.

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SUMMARY AND CONCLUSIONS

Drilling fluids or muds have a variety of functions integral to rotary drilling for oil and gas. Drilling fluids are custom formulated to perform these functions optimally under the unique conditions of each drilling operation. Therefore, no two drilling fluids are identical. Although there are more than 1,000 trade name products and generic materials available for formulating drilling fluids, 90 percent or more of the total ingredients of most water-based muds used offshore in U.S. waters consists of four materials, barite, bentonite clay, lignite and lignosulfonate. The total number of ingredients in a majority of drilling fluids is in the range of 8 to 12.

During normal exploratory drilling operations, water-based drilling mud may be discharged in small quantities with cuttings on a nearly continuous basis. Larger bulk discharges of mud may take place several times during the 2 to 6 months usually required to drill a well and a few times at the end of drilling. The total volume of mud discharged during the drilling of a well is quite variable, but usually falls in the range of 100 to 400 metric tons.

When discharged, the drilling mud forms a plume which drifts away from the rig with the prevailing current. Fractionation of the drilling mud occurs rapidly as dense particulates settle to the bottom and fine clay-size particulates and soluble materials are carried downcurrent. Substantial dilution may take place in the discharge pipe before the mud is discharged. Drilling mud concentration, measured as total suspended solids, percent transmittance, or concentration of particulate or soluble mud-associated metals, decreases rapidly with distance from the rig. Background values for total suspended solids and soluble/particulate metals concentrations are usually reached within 100-1,000 meters downcurrent of the discharge. Using ultratrace techniques for particulate barium, it is possible to trace a drilling mud plume for several km. Percent transmittance values, indicative of fine suspended clay-size particulates, usually reach background somewhat further downcurrent than suspended solids concentrations. The time required for the drilling mud plume to be diluted and dispersed to background levels is 30 to 100 minutes.

Rate of dilution to background of discharged drilling mud is affected by the rate of drilling mud discharge, current speed and turbulence, water depth and other hydrographic parameters. Dilution rate can be controlled somewhat by controlling rate of mud discharge and discharge pipe design and position in the water column.

Virtually all of the drilling mud solids and some of the soluble components eventually are deposited on the bottom under the discharge pipe and downcurrent from it. Maximum drilling mud accumulation on the bottom usually occurs a short distance downcurrent from the discharge. The most useful tracer of distribution of drilling mud in bottom sediments is barium. Surficial sediments (upper 1 cm) up to about 2 km downcurrent from the mud discharge may contain elevated concentrations of barium. Elevated concentrations of chromium, lead, and zinc may occur in bottom sediments near the discharge. Concentrations of these metals in sediments fall to background concentration at a much shorter distance from the discharge than does sediment barium concentration.

The major environmental concerns about discharge of used drilling muds to the ocean are that they may be acutely toxic or cause deleterious sublethal effects in sensitive organisms and ecosystems and that heavy metals associated with drilling muds may be accumulated by marine organisms to dangerous concentrations.

A majority of major drilling mud ingredients are biologically inert or have a very low order of acute toxicity. Of the major drilling mud ingredients, only chrome- and ferrochrome-lignosulfonates can be considered at all toxic. Their toxicity is quite low to all but a few sensitive species (e.g., some corals). Minor ingredients of some environmental concern include sodium phosphate salts, detergents, biocides (chlorinated phenols no longer are permitted for offshore disposal), chromate salts and asphalt/oil-based ingredients. Ordinarily, these materials are not used in large enough quantities to cause concern. Their concentrations should be kept low in drilling muds destined for ocean disposal. Where possible, less toxic substitutes should be used.

To date, the acute toxicity and sublethal biological effects of more than 20 used offshore-type drilling muds have been evaluated with more than 60 species of marine animals from the Atlantic, Pacific, Gulf of Mexico and Beaufort Sea. Representatives of five major animal phyla have been tested, including Chordata, Arthropoda, Mollusca, Annelida and Echinodermata. Larvae and other early life stages, and oceanic species (considered to be more sensitive than adults and estuarine species to pollutant stress) were included. In all but a few cases, acute toxicity, usually measured as 96-hr. LC50, was 10,000 ppm or higher drilling mud added. The lowest acute LC50 value was 500 ppm for stage I larvae of dock shrimp *Pandalus danae* exposed to a high density ferrochrome lignosulfonate drilling mud from Cook Inlet, Alaska. Chronic or sublethal responses were observed in a few cases at concentrations as low as 50 ppm.

Field studies of drilling mud plume dilution and dispersion reveal that drilling mud concentrations high enough to cause acute or sublethal damage to the most sensitive species and life stages should occur only in the immediate vicinity of the drilling mud discharge (to less than 1,000 m downcurrent) and only for a very brief time during bulk discharges (generally less than 2 hours). Therefore, we can conclude that adverse impacts on water column organisms of discharge of used water-based drilling muds to the ocean should be moderate and of short duration.

Benthic fauna may be vulnerable to damage from settling drilling mud and cuttings solids, through burial or chemical toxicity. Accumulation of drilling muds in coarse bottom sediments may change sediment texture and thereby affect recruitment to the benthos of planktonic larvae. At environmentally realistic levels of drilling mud in sediment, species composition of the benthic community changes toward a more silt/clay-tolerant assemblage. The species most sensitive to drilling mud in the water or sediments appear to be very sensitive to high suspended particulates concentrations. Limited field studies indicate that recovery of the benthic community from any effects of discharged drilling mud is likely to be very rapid (within a few months).

Heavy metals associated with drilling muds have a very limited bioavailability to marine animals. Chromium is the most bioavailable of the mud-associated metals. Accumulation from drilling mud of small amounts of barium, lead, cadmium and copper has been demonstrated a few times when marine animals were exposed to high concentrations of drilling muds or drilling mud ingredients. Field studies in the vicinity of drilling mud discharges have not provided any convincing evidence of metal accumulation by resident marine fauna. More research is needed on the long-term bioavailability to benthic marine organisms of metals from sediments contaminated with realistic amounts of used drilling muds.

Discharge of used water-based drilling fluids to the ocean or exposed coastal waters, where rapid dispersion and dilution is possible, poses no as yet measureable hazard of more than very localized and transitory impact on the marine environment. Even in the small temporal and spatial domain in which an adverse impact can be observed or predicted, damage is likely to be of a low order of magnitude and restricted primarily to the benthos. Metals associated with used drilling fluids have a very limited bioavailability to marine organisms, so there is little danger of food web transfer or biomagnification of mud-associated metals to commercial fishery species or Man. These conclusions apply to standard or typical water-based drilling fluids currently in use for exploratory drilling in U.S. coastal waters and outer continental shelf. Highly modified or specialized mud formulations or completely new formulations or ingredients that might be introduced may behave quite differently in the marine environment than the majority of drilling muds evaluated to date.

INTRODUCTION

Well over 27,000 oil wells have been drilled to date in the coastal and outer continental shelf waters of the United States (McAuliffe and Palmer, 1976; Monaghan et al., 1977). Offshore exploration for oil is expected to increase substantially in the coming decade as onshore reserves are depleted. There is a growing concern in this country and abroad that materials discharged from offshore oil platforms during normal drilling and production activities might have adverse short-term or long-term impacts on the marine environment.

One such material is drilling fluid (sometimes called drilling mud). Large volumes of drilling fluids are used in offshore drilling operations. Between 100 and 400 metric tons of drilling fluid may be used to drill a single well (Shinn, 1974; Hrudey, 1979). Water-based muds, but not oil-based muds, may be allowed by NPDES Permit to be discharged to the ocean. Used drilling muds are often discharged intermittently in small amounts during drilling and in bulk quantities at the end of the drilling operation (Shinn, 1974; McGuire, 1975; Ray, 1979). Approximately 110,000 tons of used drilling muds are discharged to the ocean each year (NAS, 1981).

The two major environmental concerns relating to discharge of used drilling fluids to the oceans are that: 1) the drilling fluids may be acutely toxic or produce deleterious sublethal responses in sensitive marine species or ecosystems, and 2) metals present in some drilling fluids may be accumulated by marine organisms to concentrations that could be harmful to the organisms themselves or to consumers, including Man, of fishery products.

There is a rapidly-growing body of scientific research, both published and unpublished, which addresses these concerns. The purpose of this review is to summarize and critically evaluate this scientific literature with the objective of drawing some general conclusions about the biological fate and effects of discharged used drilling muds in the marine environment.

DRILLING FLUID COMPOSITION AND USAGE

History

Drilling fluids were introduced for rotary drilling in 1913 to counteract blowouts due to insufficient hydrostatic head to balance pressures in the formations being drilled. The first drilling fluids were simply aqueous slurries of formation muds. By 1921 drilling fluid properties were being controlled through the use of additives. With this came development of techniques for testing drilling mud properties and the development of ever increasingly complex mud formulations. Drilling fluid engineering was an established field by the time the first offshore well out of sight of land was drilled in 1947. Today there are over one-thousand trade-name products available for drilling fluid formulation (World Oil, 1980), representing about 55 different generic compounds or formulations (McMordie, 1975). Ranney (1979), in his review of drilling fluids, describes over 250 drilling fluid chemicals or processes patented in the United States since 1974. Of all the chemicals available for custom-formulating drilling muds, only about 10 to 15 are actually used for mud formulation for a typical well. Four chemicals (barite, bentonite clay, lignite, and lignosulfonate) make up more than 90 percent by volume of most water-based drilling muds (Perricone, 1980). Most of the chemicals and processes available are used only when certain difficult technical problems are encountered during the drilling operation. An example of chemical modification of a drilling mud to solve specific down-hole problems will be presented below. During drilling, the mud engineer continually tests the drilling mud and adjusts the composition of the mud to counteract changes in down-hole conditions. Thus, no two muds are identical, even when taken from different depths in the same hole.

Functions

Modern drilling fluids serve several functions integral to the whole drilling operation. Drilling fluids must:

1. transport cuttings to the surface and hold them in suspension if circulation is interupted;

2. cool and lubricate the drill bit and drill pipe;
3. balance subsurface and formation pressures preventing a blowout;
4. coat the wellbore wall with an impermeable fitter cake to prevent loss of drilling fluid to permeable formations and to protect clay and shale formations from water imbibition;
5. support part of the weight of the drillstring and collars;
6. minimize corrosion to the drill string and casings;
7. provide hydraulic horsepower at the drill bit to aid in removal of cuttings.

Drilling fluids are formulated to perform these functions optimally (Monaghan et al., 1977; McGlothlin and Krause, 1980). Mud composition is changed as the relative importance of the different functions changes with well depth and formation characteristics.

Transport of cuttings can sometimes be accomplished with water alone. However, in most situations, a medium of higher viscosity is required. Ideally, the transport medium should be thixotropic. That is, it should have a relatively low viscosity while flowing, but should become highly viscous or even gel when stationary. Low viscosity is desired for ease of pumping. High viscosity and gel strength (ability to hold solids in suspension) are required to lift drill cuttings up the annulus of the hole and to prevent cuttings and weighting material from falling down the annulus when mud circulation is stopped.

The material most widely used to produce this thixotropic fluid is bentonite clay. Attapulgite and sepiolite clays are sometimes used in muds containing high salt concentrations.

With use, drilling muds may become excessively viscous due to accumulation of fine drill cuttings solids (especially clays from shale formations). Thinners are added to the mud to lower viscosity and increase the carrying capacity of the mud for drill cuttings. Chrome- or ferrochrome-lignosulfonate and lignite are the thinners most frequently used in drilling operations in U.S. coastal waters.

Density (specific gravity) of drilling mud is controlled by adding insoluble, inert powders of high specific gravity. Iron oxide, iron phosphate, and galena have been used in the past as weighting agents. Today barite (barium sulfate) is used almost exclusively as weighting agent for water-based drilling muds. Weighting of muds is required to counter high pressures that may be encountered in formations penetrated by the drill bit. If hydrostatic pressure provided by the weight of drilling mud is less than the pressure encountered in a drilled formation, fluid or gas will be forced into the drill hole from the formation, contaminating the mud system or, if pressure differential is great enough, causing a blowout. Since formation pressures tend to increase with depth, amount of barite in drilling mud is usually increased with depth drilled.

A variety of chemicals and mixtures are used to control filtration (loss of drilling fluids from the borehole to the formation) and to inhibit hydration and swelling of porous shale and clay formations. Starches, cellulose polymers, or acrylic compounds are most frequently used with bentonite clay for these purposes. Excessive loss of drilling fluid to very porous formations is combatted by addition of "lost circulation" materials which include solids of various sizes and shapes (e.g., walnut shells, mica, ground paper, leather, formica, etc.).

Some drilling muds are slightly corrosive. Corrosion of metal parts of the drill string is prevented by adding small amounts of defoamer such as aluminum stearate. Oxygen, carbon dioxide, and hydrogen sulfide from the formation or elsewhere can cause serious corrosion problems. Oxygen may be removed by addition of small amounts of sodium- or ammonium-bisulfite. Carbon dioxide is neutralized with sodium hydroxide or lime. Hydrogen sulfide problems are usually handled by addition of any of several metal salts (sodium dichromate, zinc carbonate, zinc sulfonate, zinc chromate, etc.).

Under ordinary conditions, the standard drilling mud formulation provides adequate cooling and lubrication of the drill string. However, if the borehole becomes crooked or an intentionally curved directional well is being drilled, additional lubrication may be needed. A wide variety of lubricants are available. Biodegradable vegetable oils (modified or unmodified) are used frequently where the drilling mud is destined for ocean disposal. Diesel oil may be required to free stuck pipe.

Bactericides are occasionally required to inhibit fermentation of organic polymers (especially starch) or to prevent reduction of sulfates in the mud to hydrogen sulfide by sulfate-reducing bacteria. Most muds are sufficiently alkaline to inhibit microbial activity. Currently, all bactericides used in drilling muds are regulated by the EPA under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and by specific regulations of the U.S. Geological Survey. Paraformaldehyde is one of the few products approved to date. Pentachlorophenol and other chlorinated phenols, formerly used in small amounts in some drilling muds, are prohibited for offshore use by U.S.G.S. and frequently by specific stipulation in NPDES permits. Chlorinated phenols may be used in packing fluids. These are not discharged to the ocean, but remain in the borehole at the end of drilling.

Drilling Mud-Handling System

The drilling mud system is an integral part of any modern drilling rig (Figure 1). The mud system consists of several components (Ray, 1979). Several mud tanks are situated on the rig adjacent to the drill floor. Mud holding capacity of these tanks on an offshore rig may range from 1,000 to 2,500 barrels (42,000 - 105,000 gallons). Mud is pumped from the mud tanks to a slugging tank where materials may be added to the mud as needed. The mud is pumped from the slugging tank with a high volume, high pressure pump (200 - 600 gallons per minute, 1200 - 3500 pounds per square inch) through the mud hose to the kelly (drive section of the drill pipe) on the drill floor. The mud passes under high pressure down through the drill pipe and exits through nozzles in the drill bit where it hydraulically removes cuttings.

The mud, carrying cuttings with it, then passes up through the annulus (area between drill pipe and borehole wall or casing) to the mud return line. Mud and cuttings then flow onto a series of shale shaker screens of different mesh sizes. Cuttings are retained and fall into the cuttings discharge hopper from which they are washed with a stream of water down the discharge pipe to the ocean. The mud and fine drill solids fall

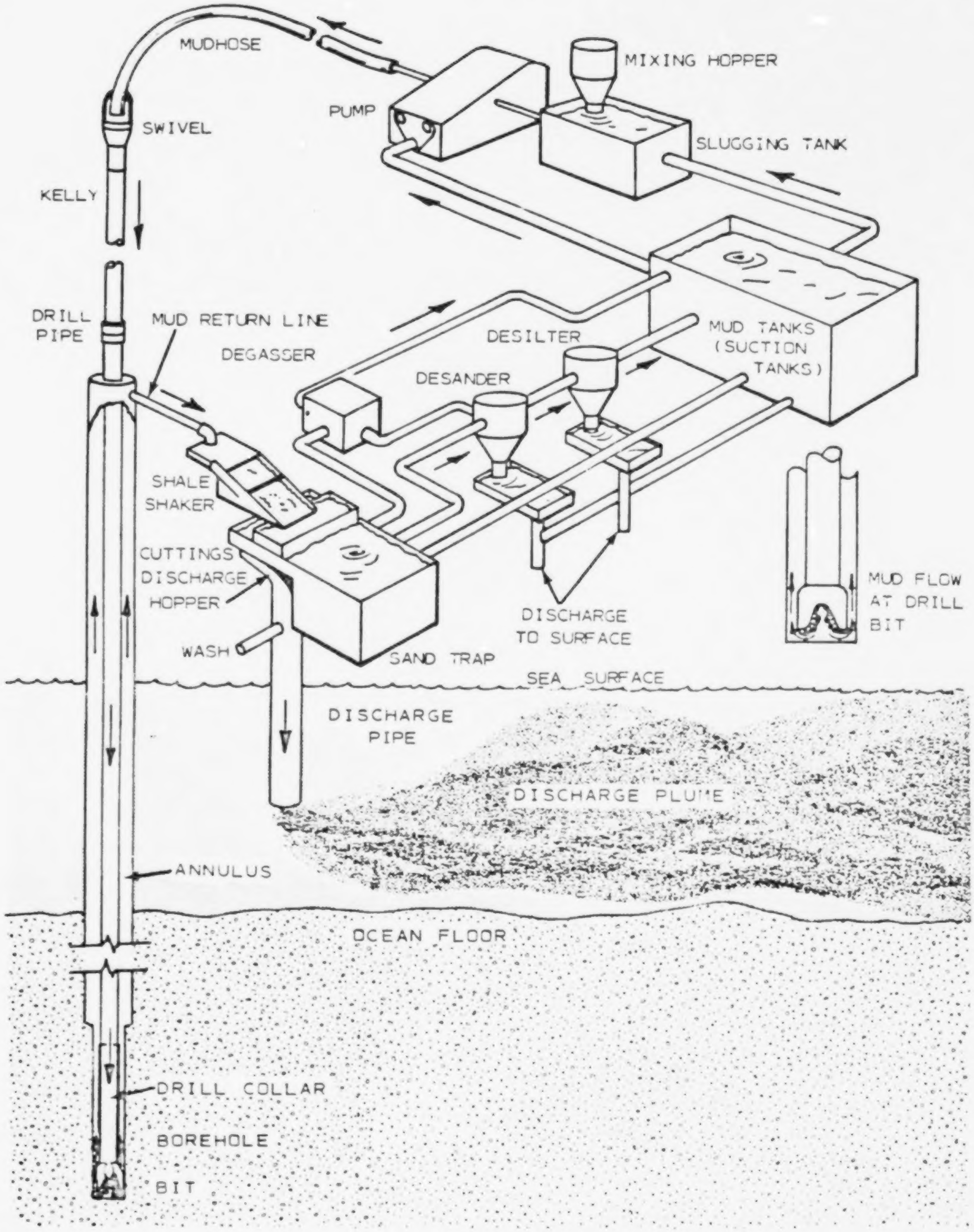
MUDHOSE
MIXING HOPPER
PUMP
SWIVEL
SLUGGING TANK
KELLY
DRILL PIPE
MUD RETURN LINE
DEGASSER
DESILTER
MUD TANKS (SUCTION TANKS)
DESANDER
SHALE SHAKER
CUTTINGS DISCHARGE HOPPER
MUD FLOW AT DRILL BIT
DISCHARGE TO SURFACE
WASH
SAND TRAP
SEA SURFACE
DISCHARGE PIPE
DISCHARGE PLUME
ANNULUS
OCEAN FLOOR
DRILL COLLAR
BOREHOLE
BIT

Figure 1. The drilling mud-handling system of a typical offshore exploratory drilling rig (From Ray, 1979).

through the shaker screens and are recirculated to the mud tanks for circulation back down the hole. On the way, they pass through a degasser, desander, desilter, mud cleaner and centrifuge which remove gases and specific size ranges of drill solids from the mud. These are discharged with washwater to the ocean.

Drilling Mud Composition

Major drilling mud ingredients and the amounts used are listed in Table 1. It is apparent that many of the major drilling ingredients are sold under a variety of trade names. As with other materials sold under several trademarks by different manufacturers, actual composition of a particular generic material (e.g. chrome-lignosulfonate) may vary slightly according to brand name. Several of the ingredients listed in Table 1 are used only occasionally in drilling muds. The concentration ranges given are the amounts typically used when that material is called for in a mud formulation.

Composition of several typical drilling fluids is summarized in Appendix I, Tables 1a - 8a. These muds were used in the Joint Bioassay Monitoring Program sponsored by the Offshore Operators Committee in compliance with NPDES permit requirements (EPA Region II) for lease areas 40 and 49 on the Middle Atlantic outer continental shelf. These drilling muds are considered typical of those used for exploratory drilling on the U.S. outer continental shelf. Several of these mud types may be used in sequence to drill a single well.

Drilling Mud Programs

Tables 2 and 3 give examples of how mud composition is changed with depth during drilling of a typical coastal or offshore well. KCl-type muds are used frequently onshore and offshore in the Canadian Arctic for shallow drilling or where shale is encountered (Hrudey, 1979). Potassium chloride (potash) in the mud acts as a flocculent and reduces shale swelling by adsorbing to the clay matrix and stabilizing the shale structure. Shale swelling from water imbibition can cause the drill stem to become stuck in the hole. KCl muds also are particularly useful for drilling through permafrost. After drilling has progressed through the permafrost zone, concentration

Table 1. Major chemical ingredients (annual consumption, 10,000 tons or more) of drilling muds, their major trade names, and quantities and concentrations used (From API, 1978).

Material/Trade Names	Consumption (Tons/Year)	Concentration Range in Mud (lb/barrel)
BARITE	1,900,000	25-700
Arcobar Baroid Bascowate Del-Bar Howcobar Imcobar Lamco Bar Magcobar Mil-Bar Ob Hevywate Pre-Mix Wate Trip-Wate		
BENTONITE CLAYS	650,000	5-35
Western Bentonite		
Arcogel Aquagel Bascogel Chemcogel Delgel Halliburton Gel Hydrogel Imco Gel Lamco Gel Magcogel Milgel Ob Bengel Premium Gel Pre-Mix Gel United Gel		
Southern Bentonite (Processed Calcium Bentonite)		
Arco Clay Baroco High Yield Clay Imco Klay Lamco Clay Ob Clay		
Processed Western Bentonite		
Basco Double-Yield Extra Hi Yield Gel Quick Gel Imcohyb Kwik-Thik Super-Col Super Gel		
ATTAPULGITE/SEPIOLITE CLAYS	85,000	10-30
Attagel Attapulgus Drilling Clay 100 Attapulgus Drilling Clay 150 Basco Salt Mud Chemco Salt Gel Del-S-Gel Geogel Imco Brinegel Lamsalgel Ob Chlorogel Salgite Salt Gel Salt Mud Salt Water Gel Sea Mud Thermogel Zeogel		
LIGNOSULFONATES	65,000	1-20
Calcium		
Kembreak Lignox		

TABLE 1. Continued)

Material/Trade Names	Consumption (Tons/Year)	Concentration Range in Mud (lb/barrel)
Chromium and/or Iron		
Archochrome Archochrome Modified Basco 300 Basco Drilflo Chemco 727 CLS Q-Broxin Rayvan Spersene Stabl-Vis Uni-Cal Ferrocal Lamco Perma Thinz Imco VC-10 Ob CLS Primix CLS		
Other Metals and Mixtures		
Arco Blend CL-CLS Imco RD 111 Ngage XKB-Thin		
SODIUM HYDROXIDE (NaOH)	50,000	1-5
SODIUM CHLORIDE (NaCl)	50,000	10-125
LIGNITE	50,000	1-25
Natural		
Arcolig Bascolig Carbonox I Kolite Del Lignite DMA Lignite Imco Lig Lamco Lig Ligco Ob Lignite Pre-Mix Lenox Superlig Tannathin		
Causticized		
Arcotone Basco Cau-Lig Causticized Lignite CC-16 DMA Ligniteu Imco Thin Imco IE Par K-Lig Ligcon Lignothin Shale Lig Super Treat Uni-Thin XKB Lig		
Chromium		
Chrome Lig Cl-Cls Del Lignite Stabil-Prop XP-20		
Zinc		
Milcon		
DIESEL OIL	30,000	3-275
SODIUM CARBONATE (Na_2CO_3)	20,000	0.1-4

TABLE 1. Continued

Material/Trade Names	Consumption (Tons/Year)	Concentration Range in Mud (lb/barrel)
LOST CIRCULATION MATERIALS	20,000	5-50
Cellophane Cotton Seed & Rice Hulls Ground Formica Mica Wood & Cane Fibers Ground Leather Bround Paper Ground Pecan & Walnut Shells		Mica Wood & Cane Fibers
STARCH		
Pregelatinized		
Arcoloid Filtrol Imcoloid Impermex My-Lo-Jel		
Chemically Modified and/or Fermentation-Resistant		
Arco Permaloid Basco Dextrid Imco Permaloid Magco Poly-Sal Starlose		
CELLULOSIC POLYMERS	12,500	0.25-5
Sodium Carboxymethyl Cellulose (CMC)		
Carbose Cellex Driscose Drispac		
Hydroxyethyl Cellulose (HEC)		
Safe-Vis Safe-Vis X		
CALCIUM CHLORIDE ($CaCl_2$)	12,500	10-200
CALCIUM HYDROXIDE/CALCIUM OXIDE (LIME) ($Ca(OH)_2$, CaO)	10,000	2-20
ASPHALT/GILSONITE	10,000	1-50
Natural, Treated, and Oxidized		
Black Magic Filter Rate Form a Seal HME Hole Coat Hydroproof Pre-Mix Wallkote Protectomagic Stabil Hole Superdril Super Lube Flow X-Pel G		
Sulfonated		
No Sluff Soltex		
ASBESTOS	10,000	1-10
Flosal Super Visbestos Shur Lift Visbestos		

Table 2. Composition of drilling muds used at four depth intervals to drill exploratory wells offshore in the Canadian Arctic (Data from Bryant, 1976 and Hrudey, 1979).

Mud Description	Mud Additive	Normal Use Range, mg/l (Bryant, 1976)	Concentration Found by Hrudey, 1979 (mg/l)
Surface Hole Mud	Bentonite	15,000 - 107,000	36,000
	Polymer	1,500 - 4,300	1,500
	Caustic	730 - 5,800	750
	Potash	29,000 - 58,000	30,000
Intermediate Hole Mud	Bentonite	15,000 - 170,000	48,000
	Polymer	1,500 - 4,300	1,500
	Caustic	730 - 5,800	750
	Barite	90,000 - 2,000,000	30,000
	Lignosulfonate	2,900 - 29,000	750
Bottom Hole Weighted Mud	Bentonite	15,000 - 107,000	69,000
	Caustic	730 - 5,800	2,500
	Barite	90,000 - 2,000,000	650,000
	Lignosulfonate	2,900 - 29,000	10,000
	Na Acid Pyrophosphate	280 - 1,500	250
Bottom Hole Weighted Mud (Drill Stem Test)	Bentonite	15,000 - 107,000	75,000
	Caustic	730 - 5,800	4,500
	Barite	90,000 - 2,000,000	1,500,000
	Lignosulfonate	2,900 - 29,000	30,000
	Na Acid Pyrophosphate	280 - 1,500	750

Table 3. Amounts of drilling mud ingredients added to drilling mud in different depth intervals during drilling of an exploratory well in the Gulf of Mexico (Adapted from Monaghan et al., 1977).

Mud Ingredient	Amount of Material Added in Depth Interval (lbs)				Total Used (lbs)
	0-2,830 ft.	2,830-6,150 ft.	6,150-7,450 ft.	7,450-9,800 ft.	
Barite	0	110,800	336,500	1,075,760	1,523,060
Bentonite	59,900	13,000	3,000	7,700	83,600
Ferrochrome Lignosulfonate	1,500	6,600	11,300	8,600	28,000
Lignite	1,500	4,500	8,000	7,600	21,600
Caustic Soda (NaOH)	8,700	4,400	10,000	55,400	78,500
Sodium Bicarbonate	0	600	0	0	600
SAPP (Sodium Acid Pyrophosphate)	300	0	0	300	600
Aluminum Stearate	0	0	0	300	300
Total Ingredients Added	71,900	139,900	368,800	1,155,660	1,418,000

of KCl in the mud is decreased by dilution and wash-out, and concentration of barite and lignosulfonate is increased (Table 2). More barite and lignosulfonate are added as the depth of the hole is increased.

Mud compositon changes during use due to addition of cuttings produced at the drill bit and due to mud washing activities on the platform to remove drill cuttings. New ingredients are added periodically to make up for that lost or diluted during mud use or to change properties of the mud. This is seen in Table 3 where amounts of materials added to the mud at different depth intervals are listed. The near-surface mud is mainly bentonite and caustic soda with small amounts of lignosulfonate and lignite. Barite and ferrochrome lignosulfonate are added in increasing amounts in subsequent depth intervals.

Drilling fluids practices and procedures follow a definite sequence during a typical exploratory drilling operation in coastal or outer continental shelf waters. The actual depths at which mud programs are changed will depend on types of formations encountered at different depths.

When exploratory drilling is performed from a floating rig which uses a marine riser system and subsurface blow out preventer, the first 150 feet or so of the hole is jetted with seawater and the resulting seawater mud is returned directly to the sea floor without being pumped to the rig. Typically, while drilling to 1,000 feet, only seawater is used as a drilling fluid and it is discharged overboard. If formation clays do not make a sufficiently viscous mud, bentonite clay is added to the system. This mud, containing water, formation clays, bentonite, and occasionally a small amount of barite and lime, is called a spud mud (Appendix I, Table 5a). Approximately 1,000 barrels of spud mud containing about 6 tons of bentonite clay may be used in a typical well. A conductor pipe (casing) is then run to 1,000 feet and cemented in place. The spud mud is discharged to the ocean.

While drilling the remainder of the hole, the drilling fluid is continuously recycled through the mud system as described above. Some drill mud is discharged with the drill cuttings. In addition, some drilling mud is discharged overboard periodically as excess amounts are generated from retention of fine drill cuttings, or addition of mud ingredients to change its properties.

Between 1,000 and 6,000 feet, the mud used may be a seawater gel mud (Appendix I, Table 6a) or a lightly treated seawater lignosulfonate mud (Appendix I, Table 7a). At about 6,000 feet the system may be converted to a freshwater lignosulfonate mud (Appendix I, Table 8a). The decision usually is based on the down-hole conditions and the type of drilling fluid required to maximize drilling speed and still protect the hole. As depth of the well increases, larger portions of barite and lignosulfonate are added. The mud may have to be treated with a variety of other additives for lubrication, filtration control, lost circulation, etc. After the well is drilled to depth, drilling mud remaining on board is usually discharged to the ocean. Typical offshore mud programs are summarized in Tables 2 and 3.

Sometimes difficulties are encountered during drilling that require a much more complex mud program. This is seen in Tables 4 and 5 which summarize the mud program for an exploratory well drilled in Mobile Bay, Alabama. This well was drilled to a greater depth (21,113 feet) than all but 0.1% of the wells drilled in 1978-1979 in the United States. Several down-hole problems were encountered while the well was being drilled (Jones, 1980). These included excessively high temperatures which caused high-temperature gelation and thermal degradation of the lignosulfonate mud system, massive anhydride (calcium sulfate) formations which resulted in serious salt contamination of the drilling fluids, and presence of hydrogen sulfide gas. The high temperatures (up to 414°F) were the most serious problem. Lignosulfonates undergo serious thermal degradation at temperatures in excess of about 330°F (165°C), causing thickening and gelation of the drilling mud (Carney and Harris, 1975; Skelly and Kjellstrand, 1966). Chromium VI in the form of sodium chromate is added to stabilize the lignosulfonate (McAtee and Smith, 1969; Skelly and Dieball, 1969). It also acts as an extender of the chrome lignosulfonate, by bringing more chrome into contact with the lignosulfonate, improving its clay deflocculating properties.

The mud program for this well can be divided into three portions, reflecting three depth intervals (and drilling conditions) in the hole. A low solids, non-dispersed mud was used in the first portion. It consisted primarily of clays and caustic soda in water with increasing amounts of barite added with depth for weighting. Small amounts of several additives were added to combat stuck pipe, foaming, lost circulation, etc. This program was continued down to about 9,600 feet. The mud system was converted

Table 4. Time/depth history of drilling mud ingredients usage during drilling of Mobil Oil Company's #1-76 well in Mobile Bay, Alabama. Units are one thousand pounds (Adapted from Jones, 1980).

Date Interval Depth Interval (feet) Mud Component	11/18-12/11 650-3,110	12/12-2/5 2,514-5,950	2/6-3/1 5,950-5,962	3/2-3/25 5,963-9,978	3/26-4/18 10,101-13,761	4/19-5/12 13,940-14,553	5/13-6/5 14,567-14,568	6/6-6/29 14,598-15,824	6/30-7/23 16,000-17,917	7/24-8/16 18,023-19,374	8/17-9/8 19,374-20.618	9/9-10/13 20,680-21,113	10/14-11/16 21,100-20,550	11/17-12/16 20,550-12,500	12/17-12/27 12,500-12,300	405 Days 21,113 Total
1. Barite	63.6	73.8	99.4	114.8	42.4	136.0	116.0	62.1	264.0	352.1	530.2	188.0	146.2	122.1	80.0	2,390.1
2. Bentonite Clay	80.6	21.2	24.2	52.5	57.2	60.7	61.7	53.4	43.8	47.6	45.7	124.1	8.8	11.4	-	692.7
3. Caustic Soda (NaOH)	30.6	16.1	20.0	20.0	43.1	22.4	2.8	13.9	29.1	37.2	20.0	25.2	10.0	15.8	6.7	312.9
4. Viscosifiers	9.9	-	0.75	-	-	-	-	-	-	-	-	-	-	-	-	10.65
5. Attapulgite Clay	55.5	-	9.0	-	-	-	-	-	-	-	-	-	-	31.6	12.9	109.0
6. Na Polyacrylamide Polymer	0.02	-	-	0.03	-	-	-	-	-	-	-	-	-	-	-	0.05
7. Na Acid Pyrophosphate (SAPP)	3.1	1.2	2.0	-	0.9	0.2	5.1	2.9	-	-	-	-	-	-	-	15.4
8. Soda Ash (Na_2CO_3)	7.0	13.4	-	-	5.3	12.98	5.2	1.8	-	-	3.9	1.2	0.1	-	-	50.7
9. Lost Circulation Material	2.08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.08
10. Detergent	1.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.3
11. Lignite	6.0	12.0	4.3	11.0	10.5	12.0	5.6	-	-	-	-	12.5	1.5	-	1.0	76.4
12. Polyanionic Cellulose Polymer	0.5	-	1.7	0.5	0.2	0.85	-	0.55	2.5	5.6	1.5	3.05	-	-	-	16.95
13. Spotting Fluid	10.0	-	-	-	-	-	-	-	-	-	-	8.15	-	-	-	18.15
14. Emulsifiers	-	0.17	-	-	-	-	-	-	-	-	-	-	-	-	-	0.17
15. Surfactant	-	0.16	0.41	0.45	0.45	-	-	-	0.12	-	2.15	-	-	-	0.04	3.78
16. Ground Pecan Shells	-	-	2.25	0.30	1.38	0.82	-	2.20	0.98	3.42	-	1.30	-	-	-	12.65
17. Lubricant	-	-	7.54	-	-	-	-	6.59	-	1.10	1.24	0.37	-	-	-	16.84
18. Ground Mica	-	-	4.75	-	-	-	-	1.80	-	0.75	-	3.35	-	-	-	10.65
19. Defoamant	-	-	-	0.24	0.31	-	-	-	-	-	-	-	-	-	-	0.55
20. NaPolyacrylate Blend	-	-	-	0.15	0.06	-	0.05	-	-	-	-	-	-	-	-	0.26
21. Aluminum Stearate	-	-	-	0.15	0.45	-	-	-	-	-	0.15	-	-	-	0.82	1.57
22. Ferrochrome-Lignosulfonate	-	-	-	-	11.65	12.65	11.10	9.95	-	-	5.90	24.15	3.05	3.60	-	82.25
23. Sodium Chromate	-	-	-	-	-	0.90	1.00	2.90	3.90	5.20	4.80	8.00	-	-	-	27.5
24. Ferrochrome-Lignosulfonate/NA Dichromate	-	-	-	-	-	-	4.50	8.25	25.25	24.30	21.50	5.65	2.15	-	4.10	95.7
25. High Temp. Ferrochrome-Lignosulfonate	-	-	-	-	-	-	-	2.95	9.20	9.25	12.30	19.50	1.00	1.40	-	55.6
26. Na Polyacrylate Polymer	-	-	-	-	-	-	1.00	5.05	-	-	-	-	-	-	-	6.05
27. Lime ($Ca(OH)_2$)	-	-	-	-	-	-	-	-	2.40	6.25	5.70	20.55	1.80	2.00	-	38.7
28. Water-Disperable Asphalts	-	-	-	-	-	-	-	-	-	-	6.10	3.50	-	-	-	9.60
29. H_2S Scavenger	-	-	-	-	-	-	-	-	-	-	3.00	-	5.15	2.10	-	10.25
30. Sulfonated Asphaltene	-	-	-	-	-	-	-	-	-	-	-	5.10	-	-	-	5.10
TOTAL	269.60	138.03	176.10	200.12	174.10	259.32	214.05	174.34	381.25	492.77	664.15	454.47	179.75	190.00	105.56	4,073.6

Table 5. Description of drilling mud ingredients used in Mobil Oil Company's #1-76 well in Mobile Bay, Alabama. Numbers refer to numbers in the mud component column of Table 4 (From Jones, 1980)*.

1. Imco Bar. Barite ($BaSO_4$); weighting agent.
2. Imco Gel. Western bentonite clay (sodium montonorillonite); viscosifier.
3. Caustic soda (NaOH); pH control agent.
4. Flosal & Imco Shurlift. Acid-soluble chrysotile asbestos fibers; viscosifier.
5. Imco Brinegel. Attapulgite clay; viscosifier for salt-water muds.
6. Imco Floc. Polymeric sodium polyacrylamide; flocculant.
7. SAPP. Sodium acid pyrophosphate; calcium precipitant.
8. Soda ash. Sodium carbonate (Na_2CO_3); counteract calcium sulfate
9. IMCO KWIK-SEAL. A blend of nut shells, cellophane flakes, paper, and mica; lost circulation material.
10. IMCO MD. Modified alkanolamid and sodium acid pyrophosphate buffered in an aqueous base; detergent.
11. IMCO LIG. North American lignite coal. Thinning agent.
12. DRISPAC. High moleculer weight polyanionic cellulosic polymer; fluid loss controler and viscosifier.
13. IMCO SPOT. Weighted mixture of calcium oleate and asphalt; spotting fluid, used to free stuck drill pipe.
14. IMCO SWS. Blend of sulfonated fatty acid derivatives; emulsifier.
15. IMCO DEFOAM-L Phosphoric acid tributyl ester; surfactant.
16. IMCO PLUG. Ground pecan shells; lost circulation material.
17. IMCO LUBE 106. Blend of glycerol mono-oleates and mixed long chain alcohols; lubricant.
18. IMCO MYCA. Ground mica; lost circulation material.
19. IMCO FOAMBAN. Blend of phosphoric acid tributyl ester, alcohol, and refined hydrocarbon carrier; defoamant.
20. IMCO GELEX. Sodium polyacrylates; bentonite extender.
21. Aluminum stearate. Insoluble aluminum salt of octadecanoic acid; defoamant.
22. IMCO VC-10. Ferrochrome lignosulfonate; dispersing and thinning agent.
23. Sodium chromate. $Na_2CrO_4 \cdot 10H_2O$; prevents high temperature gellation of water-based drilling mud.
24. IMCO RD-III. Blended ferrchrome lignosulfonate containing added sodium bichromate; heat-stable dispersant and thinning agent.
25. IMCO POLY-Rx. Blend of lignosulfonates, polymers, and sodium carbonate; heat-stable dispersant thinning agent.
26. IMCO SP-101. Sodium polyacrylate polymer; fluid loss agent.
27. Lime. $Ca(OH)_2$; source of calcium for spud and lime muds.
28. IMCO HOLECOAT. Blend of water-disperable asphalts; lubricant and fluid loss agent.
29. IMCO SULF-X II. Mixture of zinc sulfonate, sodium nitrilotriacetic acid, and zinc carbonate; hydrogen sulfide scavenger.
30. Soltex. Sulfonated asphaltene; lubricant and hole stabilizer.

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*, Analyses by Dr. Thomas Gilbert (New England Aquarium, personal communication) of hydrocarbons in several samples of Mobile Bay drilling muds revealed high concentrations of petroleum (up to 5,000 ppm) with a hydrocarbon composition similar to that of diesel oil.

to a dispersed system between 9,000 and 10,000 feet by addition of lignite and then ferrochrome lignosulfonate. This program was continued down to about 14,500 feet. Large anhydride formations were encountered in this segment. SAPP, soda ash and other chemicals were added to counteract this problem. By 14,500 feet, the mud was a heavily treated lignosulfonate mud as more and more chemicals were added to counteract problems. As temperatures increased, temperature extenders (Gelex, chromates, polymers) were added in increasing amounts. Hydrogen sulfide was encountered near 19,000 feet, requiring addition of an H_2S scavenger.

In all, thirty-one products (including diesel oil) were used to formulate the muds used in this drilling mud program. This is two to three times the number of materials used in most mud programs. It should be pointed out that the State of Alabama had prohibited all discharges from this exploratory rig to Mobile Bay. The drilling muds were never intended for ocean disposal. They were disposed of on land. However, drilling mud from this well has been used extensively in the marine toxicology research discussed elsewhere in this review.

Trace Metals in Drilling Muds

The ingredients in drilling muds of major environmental concern are the trace metals. Many elements, such as calcium, magnesium, aluminum, sodium, potassium, chlorine, etc., are normal major components of clays and soils, have a relatively low toxicity, and, therefore, are of little environmental concern in drilling muds, with few exceptions (e.g., potassium in KCl muds poses a toxicological problem when the mud is discharged to fresh water [Sprague and Logan, 1979]).

Accurate and precise analysis of metals in used drilling muds is hampered by the fact that most drilling muds are extremely heterogeneous and many of the metals are present in the form of extremely insoluble metal salts (Hrudey, 1979; Kalil, 1980). Partly because of these problems, but also because of variability in the purity of major ingredients like barite, bentonite and lignosulfonate, published values for metals concentrations in used drilling muds are quite variable (Table 6; Appendix I, Tables 2a-9a). The metals of major concern are barium, chromium, cadmium, copper, iron, mercury, lead and zinc. Arsenic, nickel, vanadium, and manganese also

Table 6. Trace metal concentrations in drilling muds from different sources. Concentrations are in mg/kg dry weight (ppm).

Drilling Mud	Ba	Cr	Cd	Cu	Fe	Hg	Pb	Zn	Others	References
48 Samples Canadian Arctic Muds	NA	0.1-909	NA	<0.05-250	0.002-9,250	NA	NA	0.06-1,700		Siferd, 1976
3 Barite CLS[1] Muds	NA	NA	0.16-54.4	6.4-307	NA	0.2-10.4	0.4-4,226	6.6-12,270	3.8-19.9 Ni	Nelson et al., 1980
2 Mid-Atlantic CLS Muds	229,100-303,700	1,112-1,159	0.6-0.8	5.8-7.7	NA	<0.05	102.6-218.5	36.0-48.4	1.8-2.3 As 13.5-17.0 Ni 22.7-28.0 V	Ayers et al., 1980
3 Mid-Atlantic CLS Muds	823-19,300	57-90	<2	NA	NA	<1-2.8	<10-241	101-197	20-33 Ni 14-20 V	EG&G, 1980
Baltimore Canyon CLS Mud	202,000	850	NA	20	19,000	NA	NA	NA		Liss et al., 1980
Gulf of Mexico CLS Mud	133,00	200	NA	280	16,000	NA	NA	NA		Liss et al., 1980
Gulf of Mexico Spud Mud[2]	NA	51	0.51	NA	NA	NA	NO	NA		Page et al., 1980
Gulf of Mexico High Density CLS Mud[2]	NA	257	0.78	NA	NA	NA	1.3	NA		Page et al., 1980
Gulf of Mexico Mid-Density CLS Mud[2]	NA	396	1.70	NA	NA	NA	5.0	NA		Page et al., 1980
Mid Atlantic Low-Density CLS Mud	NA	596	1.18	NA	NA	NA	NA	NA		Page et al., 1980
Gulf of Mexico Seawater CLS Mud	NA	485.2	3.0	48.2	NA	NA	179.4	251.4		McCulloch et al., 1980
Gulf of Mexico Spud Mud[2]	NA	10.9	3.5	30.2	NA	NA	134.2	297.3		McCulloch et al., 1980
Gulf of Mexico High Density CLS Mud	NA	229.9	10.9	118.8	NA	NA	209.5	274.5		McCulloch et al., 1980
Gulf of Mexico Mid Density CLS Mud[2]	NA	416.7	19.2	127.0	NA	NA	915.3	604.8		McCulloch et al., 1980
2 CMC[3]/Gel Muds Alaska[4]	4,400-6,240	28-63	<0.5-0.6	6.4-10.4	NA	0.017-0.031	2.4-12.8	42-64		Tornberg et al., 1980
XC Polymer Muds Alaska (20)[4]	720-1,120	66-176	<0.5-1.5	10-16	NA	0.015-0.070	5.6-56	49-110		Tornberg et al., 1980
XC Polymer/Unical Muds Alaska (6)[4]	NA	56-125	NA	2.8-17.0	NA	0.028-0.217	9-117	198-397		Tornberg et al., 1980
CLS Muds Alaska (4)[4]	800-7,640	121-172	<0.5	10-12	NA	0.03-0.07	16.4-56.0	49-56		Tornberg et al., 1980
Gulf of Mexico CLS Mud	90,000	500	NA	43	27,000	NA	91	370	400 Mn	Trefry et al., 1981
Mobile Bay Treated CLS Mud	NA	5,960	NA	47	10,100	NA	22	540	290 Mn	Trefry et al., 1981

1. CLS, chrome lignosulfonate; 2. The same muds were analyzed by Page et al., 1980 and McCulloch et al., 1980; 3. CMC, carboxymethylcellulose;
4. Concentrations given on a wet-weight basis; 5. NA, not analyzed.

may be present at elevated concentration in some muds. Some of these metals are added intentionally to drilling muds as metal salts or organometallic compounds. Others are trace contaminants of major mud ingredients (Table 7).

Barium in drilling fluids is almost exclusively from barite (barium sulfate) added to drilling mud as a weighting agent. Bentonite clay also may contain some barium. Barium sulfate has a specific gravity of 4.1 - 4.3 g/cc and a solubility in seawater of approximately 224 μg $BaSO_4$/ℓ (132 μg Ba/ℓ) (Desai et al., 1969). Chow (1976) estimated the solubility of barium in surface seawater to be 46 μg/kg based on a normal seawater sulfate concentration of 28 mM. Recent analyses of surface waters of the Atlantic and Pacific oceans give values generally in the range of 4-11 μg/kg dissolved barium (Chan et al., 1976; Chow, 1976; Chow and Snyder, 1980). Thus seawater is slightly under-saturated with respect to barium.

Dissolved organic materials in seawater may increase the apparent seawater solubility of barium somewhat, probably by binding the barium in a soluble complex (Desai et al., 1969). Thus Liss et al. (1980) observed dissolved barium concentrations of 0.021-0.103 mg/ℓ in seawater suspensions of two synthetic drilling muds. Three samples of used drilling mud analyzed by Liss et al. (1980) contained 15-18 mg/ℓ barium in the liquid phase. Presumably much of this barium was complexed to soluble organics (e.g. lignosulfonate) in the mud.

The amount of barium sulfate added to a drilling mud may vary from 0 to about 700 lb per barrel (0-2 kg/liter). Barium represents up to 30 percent of the weight of dry ingredients in the mud (Ayers et al., 1980a). Because of the extremely low solubility of barite in seawater, nearly all the barium discharged to the ocean remains in particulate form as barite or barite-clay complex (Trefry et al., 1981).

Chromium in drilling muds is derived primarily from chrome- and ferrochrome lignosulfonates added to drilling muds as deflocculants and thinners. Chromium concentration of several lignosulfonates is listed in Table 7. In addition, Beckett et al. (1976) reported the following values for total chromium for three brands of lignosulfonate: Q-Broxin (ferrochrome lignosulfonate), 19,500 ppm (mg/kg); Spersene (chrome lignosulfonate),

Table 7. Trace metal composition of drilling fluid components. Concentrations are in mg/kg dry weight (ppm).

Material	Ba	Cr	Cd	Cu	Fe	Hg	Pb	Zn	Others	Reference
Barite (vein deposits)	NA[1]	NA	0.6-32	0.6-560	200-59,000	0.8-28	<2-3,370	<0.2-9,020	0.008-170 As 15-41 Ni	Kramer et al., 1980
Barite (bedded deposits)	NA	NA	0.5-0.7	5.4-7.6	2,500-6,000	0.13-0.26	1-1.8	6-10	1.4-1.8 AS 0.5-5.7 Ni	Kramer et al., 1980
Barite	NA	54	NA	44	34,900	NA	286	1,270		Beak Cons., 1974
Barite	55,000	3.6	NA	NA	NA	0.054	<1.0	NA		ECOMAR, 1978
Barite	NA	0-3	NA	4-30	30-1,500	NA	0	NA		Perricone, 1980
Barite	NA	<10	<2	NA	NA	<1	<10	<5		Ayers et al., 1980
Barite	NA	2.5	10.0	NA	NA	14.2	890	2,100	25.7 As	Crippen et al., 1980
Barite	501,000	NA	NA	91	21,700	NA	1,370	2,750		Trefry et al., 1981
Barite	NA	11	NA	290	9,500	NA	19	19		Trefry et al., 1981
Bentonite Clay	560	3.3	NA	NA	NA	NA	NA	NA		ECOMAR, 1978
Bentonite Clay	NA	<10	<2	NA	NA	<1	<10	57		Ayers et al., 1980
Bentonite Clay	NA	1.5	0.6	NA	NA	0.02	22.5	31.0	0.7 As	Crippen et al., 1980
Chrome Lignosulfonate	64	24,500					<1.0			ECOMAR
Chrome Lignosulfonate	NA	925	1.4	NA	NA	0.02	2.5	5.9	0.25 As	Crippen et al., 1980
Chrome Lignosulfonate	NA	39,100	NA	8	1,250	NA	10	17	1,440 Mn	Trefry et al., 1981
Chrome Lignosulfonate/Lignite 1/1	NA	14,600	<2	NA	NA	<1	<10	15		Ayers et al., 1980
Ferrochrome Lignosulfonate (Peltex)	NA	16,100	NA	11	36,700	NA	<0.25	1.2		Beak Cons., 1974
Iron Lignosulfonate (DFE 506)	NA	53	NA	3.3	74,500	NA	<0.25	1.8		Beak Cons., 1974
Lignite	NA	300	5.5	NA	NA	NA	<1.0	NA		ECOMAR, 1978

NA = not analyzed

5,000 ppm; Unical (chrome-modified lignosulfonate), 44,500 ppm. Of the other major mud ingredients, barite and lignite also may contain some chromium. In addition, inorganic chromium salts are sometimes added to drilling muds for such purposes as high temperature stabilization of lignosulfonate, corrosion control, and H_2S scavenging. Typical used offshore drilling muds may contain 0.1 to about 1,200 mg/kg dry weight and exceptionally to about 6,000 mg/kg total chromium (Table 6; Appendix I, Table 2a - 8a).

Lignosulfonates are by-products of the sulfite pulping process in paper manufacturing. The spent sulfite liquor is evaporated and desugared (Perricone, 1980). The desugared liquor is then treated with sulfuric acid and sodium dichromate. The sodium dichromate oxidizes the lignosulfonate and cross-linking occurs. The hexavalent chromate is reduced by the lignosulfonate to the trivalent (chromic) state and complexes with the lignosulfonate. Chromium is probably coordinated with lignosulfonate through phenolic oxygens, sulfonate groups, and carboxylic acid groups (Knox, 1978) and is not readily exchangeable (McAtee and Smith, 1969; Skelly and Dieball, 1969).

Soluble chromates (Cr VI) are sometimes added to drilling muds to improve their thermal stability and for corrosion protection. Usually, these are chemically reduced to the more stable trivalent state (Cr III) (Skelly and Dieball, 1969; Moseley, 1980) in the presence of chrome lignosulfonate, lignite, and other organic material in drilling mud. Once chromium is reduced from the +6 to the +3 valency state in seawater, it is not readily oxidized back to the +6 valency state under normal conditions (Fukai and Vas, 1969; Schroeder and Lee, 1975).

Chrome-and ferrochrome lignosulfonates are very soluble in water. Knox (1978) reported that 500 g of ferrochrome lignosulfonate will dissolve in one liter of water without precipitation, even at a pH of 10 typical of drilling mud. When initially prepared, much of the chromium in ferrochrome lignosulfonate is associated with low molecular weight material (MW 1000-4000) (Liss et al., 1980). With aging, particularly at alkaline pH characteristic of drilling muds, much of the metal becomes associated with high molecular weight material (about 100,000 MW) (Knox, 1978; Liss et al., 1980). It appears that, in the presence of alkali, ferrochrome lignosulfonates are converted to lignosulfonate polymers highly cross-linked by the metals or to polymerized chromium and hydrous oxides incorporating lignosulfonate complexes (Liss et al., 1980).

In a drilling mud during normal usage, chrome- or ferrochome-lignosulfonate becomes adsorbed to the clay particles. It is thought that the metals adsorb to the clay by displacing the sodium in the clay matrix. The lignosulfonate is attached to the clay by being bound to the adsorbed metals (Knox, 1978). The rate of the adsorption process is slow at room temperature, but is accelerated by high temperature (McAtee and Smith, 1969; Skelly and Dieball, 1969; Knox, 1978).

Thus, in a chrome- or ferrochrome-lignosulfonate drilling mud that has been used for an extended period of time at moderate down-hole temperatures, much of the chromium will be associated with the clay portion. However, significant amounts of chromium may remain in the aqueous phase, presumably still complexed with soluble lignosulfonate (Table 8). Liss et al. (1980) reported 9 - 45 mg/ℓ total chromium in the liquid phase of used drilling fluid samples containing 200-850 mg/kg total particulate chromium. Similar results have been obtained for other used chrome lignosulfonate drilling muds by Neff et al. (1980) and Page et al. (1980).

Concentrations in used drilling muds of cadmium, copper, mercury, lead and zinc are extremely variable (Table 6; Appendix I, Tables 2a - 9a). Most of these metals are present as trace impurities in several major drilling mud ingredients (Table 7).

Cadmium and mercury are of particular concern because of their high toxicity to marine organisms and potential for transfer through aquatic food chains to Man (Hiatt and Huff, 1975; Calabrese et al., 1977). These metals are present in drilling fluids almost exclusively as trace contaminants of barite. As can be seen in Table 7, barite from different sources may contain

Table 8. Dissolved (aqueous phase) metal concentrations in drilling mud samples taken at several depths from the Imperial Oil Company, ADGO F-28 well offshore the MacKenzie River Delta, Beaufort Sea, Canadian Arctic. All values are in mg/liter (From Beak Consultants, 1974).

Metal	Depth (feet)			
	4,000	6,000	7,000	8,000
Cadmium	<0.05	<0.05	<0.05	<0.05
Chromium	3.6	6.1	3.5	6.0
Copper	<0.05	<0.05	<0.05	<0.05
Iron	2.8	5.3	-	5.3
Lead	<0.25	<0.25	<0.25	<0.25
Zinc	0.06	0.30	0.15	0.18
Sodium	3,800	1,060	780	900
Potassium	2,700	150	70	70
Calcium	90	3.7	2.5	2.6
Magnesium	34	2.1	1.2	1.9

0.5 - 32 ppm cadmium and 0.13 to 28 ppm mercury. These and other metal contaminants of barite are present almost exclusively as extremely insoluble sulfides (Kramer et al., 1980). As a result, very little of these metals appears in the soluble or aqueous phase (Table 8). Kramer equilibrated 1 g each of low- and high-trace metal barite with 100 g seawater and measured soluble metal concentrations in 0.45μm-filtered samples of the water (Table 9). In samples equilibrated with low trace metal bedded barite, all aqueous metal concentrations were at or below normal oceanic levels. In seawater equilibrated with high trace metal vein barite, concentrations of soluble mercury, lead and zinc were significantly higher than open ocean concentrations. Addition of bentonite clay (a normal ingredient of drilling muds) reduced aqueous mercury concentrations to below oceanic levels.

Mercuric sulfide and most other metallic sulfides are quite immobile once deposited in bottom sediment because of their low aqueous solubility. Although mercury from mercuric sulfide can be methylated to highly mobile and toxic methyl mercury compounds by sediment bacteria, speed and efficiency of this transformation is only 10^{-3} times that of methylation of ionic Hg^{+2} (Fagerstrom and Jernelov, 1971). Because of the low concentration of mercury in most drilling mud samples, and its presence there primarily in the form of insoluble mercuric sulfide, discharge of drilling muds to the ocean does not appear to represent a significant route of entry of mobile mercury compounds to the marine environment.

Bentonite clay and chrome lignosulfonates may contribute small amounts of cadmium, copper, lead, and zinc to drilling muds (Table 6). In addition, pipe thread compound (pipe dope) and drill collar dope (used to lubricate the threads where two sections of drill pipe or pipe and drill collar are joined together and make the union electrically conducting) may contain high concentrations of metallic lead, zinc and copper. According to Ayers et al. (1980a), drill pipe dope contains 15 percent copper and 7 percent lead. Drill collar dope contains 35 percent zinc, 20-30 percent lead and 7 percent copper. As much as 250 kg pipe dope and 160 kg drill collar dope may be used during drilling of a single well. Although these dopes are not added directly to the drill mud, small

Table 9. Concentrations of heavy metals in solution in seawater equilibrated with solid barite (barium sulfate) containing low or high concentrations of trace metals. Concentrations are in μg/kg (parts per billion). (From Kramer et al., 1980).

Sample	Metal						
	Hg	Pb	Zn	Pd	Cu	Ni	As
Ocean seawater[1]	0.03	~1	<1	0.03	<2	~1	~1
Low trace metal							
Bedded barite	<0.01-0.14*	<1-1	<0.1	<0.1-1.4	<1-1.9	2-5	<0.2
Vein barite	<0.01-0.32*	50-200	7-290	0.4-5	1-4.3	6.6-10	<0.2

1. From Hogdahl (1963). The trace elements in the ocean. A bibliographic compilation. Central Inst. Indust. Res. Blindern, Oslo, Norway.

* with bentonite <0.01-0.01.

amounts get into it. Metals from this source are in the form of fine metallic granules and are very unevenly distributed in the mud. Finally, inorganic zinc salts as zinc carbonate, zinc chromate, or zinc sulfonate may be added to drilling muds as H_2S scavengers. In such cases zinc is precipitated as zinc sulfide.

A few analyses for arsenic, nickel, vanadium, and manganese have been performed on drilling muds and mud ingredients (Tables 6 and 7). Arsenic may be present in drilling muds at concentrations near 2 mg/kg, nickel at 4-30 mg/kg and vanadium at 14 - 28 mg/kg. Manganese may occur at much higher concentrations (290 - 400 mg/kg). Arsenic, nickel, and possibly also vanadium are introduced primarily with barite. Chrome lignosulfonate may contain high concentrations of manganese. Marine sediments also typically contain high concentrations of manganese.

Concentrations of iron are high in most drilling mud samples (Table 6). Concentrations in excess of 10,000 mg/kg (1%) appear common. Bentonite and several other clays are 2 - 4 percent iron by weight (Ayers et al., 1980a). Of course, ferrochrome- and iron-lignosulfonates contain high concentrations of iron.

Other Characteristics

Most used offshore drilling fluids have an alkaline pH due to added NaOH and Na_2CO_3. Typical pH is between 8 and 11 (see Appendix I, Tables 2a - 8a). Mud weight or density usually varies between 9 and 18 lb. per gallon (1.07 to 2.15 kg/liter). Chemical oxygen demand of whole used mud is often in the range of 1,000 - 20,000 mg/liter and seems to be related to concentrations of organic compounds in the mud (Beak Cons., 1974).

Total organic carbon concentration may vary from 30 to 10,000 mg/l mud, depending on original mud composition (Strosher, 1980). About three-fourths of the organic carbon in used drilling muds is attributable to unaltered mud additives. Petroleum hydrocarbons, either added intentionally as diesel oil or asphalt or from strata penetrated by the drill, may account for 5 - 10 percent of the TOC. Chrome lignosulfonate undergoes some decomposition and degradation under conditions of high temperature, alkalinity and pressure characteristic of a deep hole (Carney and Harris, 1975; Knox, 1978). Thermal degradation of chrome-lignosulfonate is accelerated at temperatures above about 330°F (165°C) (Simpson, 1967). The lignin of chrome lignosulfonate is a polymer of an alcohol-substituted phenyl propane and its degradation products may include phenolic compounds such as vanillin and isoeugenol (Carney and Harris, 1975). Other organic compounds added to some muds (lignite, carboxymethylcellulose, starch, organic dispersants, emulsifiers, lubricants, etc.) may be subject to temperature/pressure degradation and lead to production of a variety of organic by-roducts. The important conclusion to draw from this discussion is that drilling muds change in chemical composition and physical properties during normal usage. A newly-formulated or laboratory-mixed "synthetic" mud will be quite different physically and chemically from a drilling mud that actually has been used for an extended period of time in an offshore drilling operation. By inference, toxicity of newly-formulated or synthetic and real used drilling muds can be expected to be quite different.

FATE OF DRILLING FLUIDS DISCHARGED TO THE OCEAN

Discharge Practices

During normal exploratory drilling operations several drilling mud and cuttings-related effluents are discharged to the oceans. Typical discharges and discharge rates from an offshore platform are summarized in Table 10. The only more-or-less continuous discharge during normal drilling is from the shale shakers which remove drill cuttings from the mud that has returned from down-hole. Although most of the mud is removed from the cuttings during passage through the shale shakers, discharged cuttings may contain 5-10 percent drilling mud. The amount of drill cuttings produced per day depends on the vertical distance drilled that day and the diameter of the drilled hole. Hole size decreases with increasing depth drilled (Monaghan et al., 1977; Ray, 1979). A typical bore hole may be 36 inches in diameter for the first 500 feet and diameter may be reduced at about five depth intervals to about 6.5 inches at 15,000 - 20,000 feet. The hole is lined with steel casing which is held in place with cement injected into the annulus between the casing pipe and the hole wall. During emplacement and cementing of casing, drilling is stopped. The drill may have to be changed every 20-100 hours of operation. To do this the complete drill string must be removed from the hole, which may take 12 hours. Drilling may have to be stopped temporarily if problems are encountered or for normal operations like testing, logging, and well surveys. Drilling may actually occur only one-third to one-half the time during a two-three month drilling operation (Ray, 1979; Ray and Meek, 1980).

Therefore, drilling and as a result cuttings discharge are not continuous. In addition, volume of cuttings discharged per day while drilling is going on decreases as the depth of the well increases and casing diameter decreases. Temporal pattern of a typical cuttings discharge is shown in Figures 2 and 3 (Ray and Meek, 1980). Large volumes of cuttings are released directly to the sea floor without being returned to the rig during the jetting and spudding in of the surface hole. After returns to the rig are established, rate of cuttings discharge from the shale shakers decreases almost logarithmically with time during the remainder of

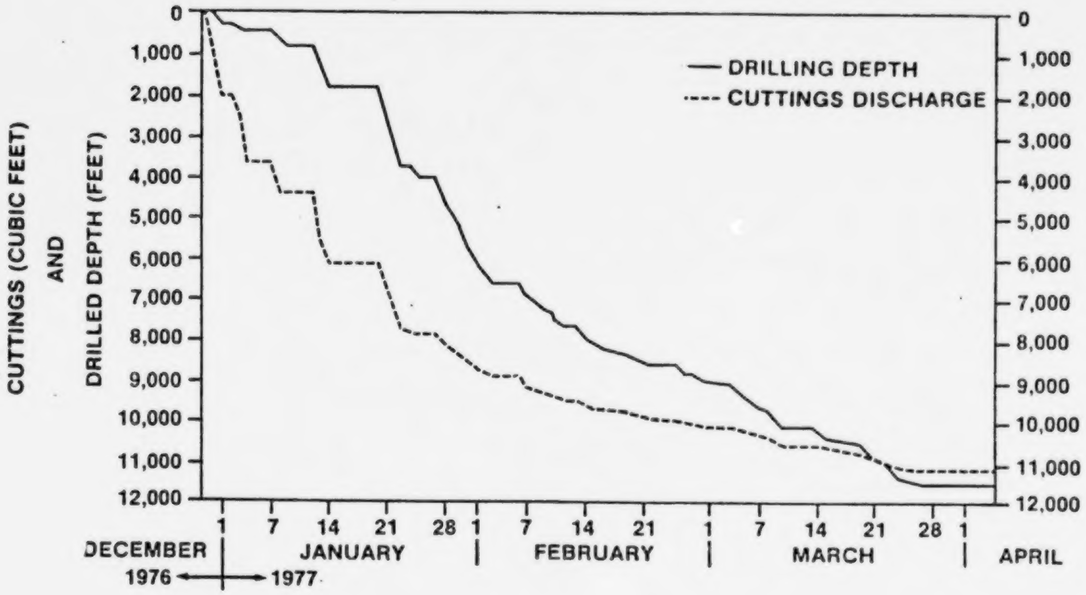


Figure 2. Relationship between drilling depth, drill cuttings produced and time during exploratory drilling on Tanner Bank, California (From Ray and Meek, 1980).

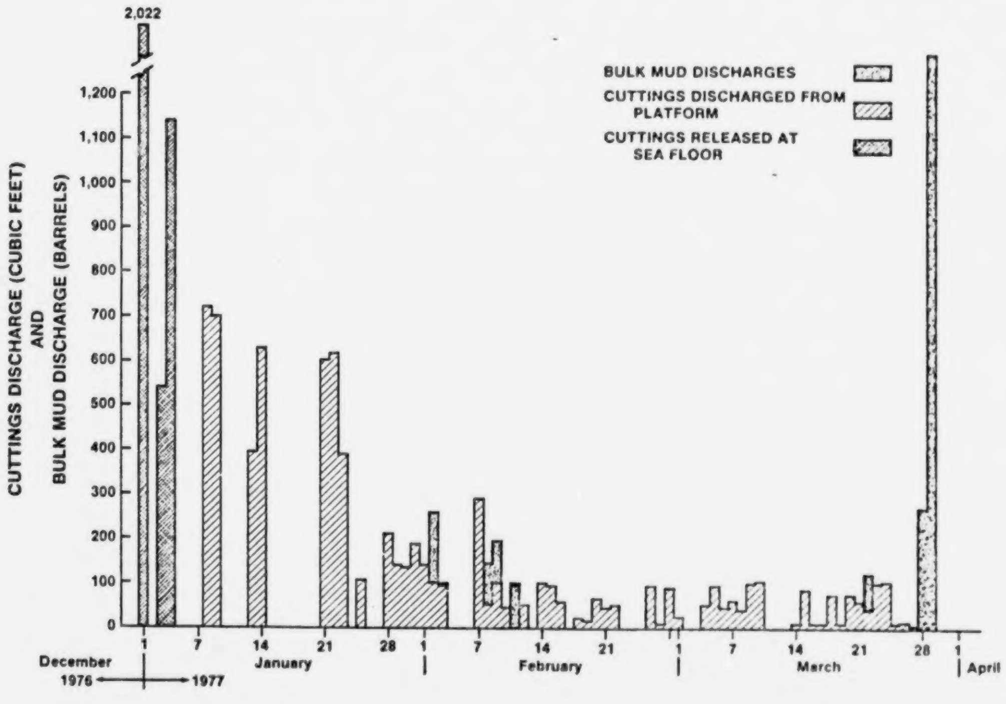


Figure 3. Volumes of bulk drilling mud and cuttings discharges each day during drilling of an exploratory well on Tanner Bank, California (From Ray and Meek, 1980).

the drilling operation. For the Tanner Bank, California exploratory well studied by Ecomar (1978) and Ray and Meek (1980), total volume of cuttings produced and discharged during drilling to 3,419 meters (11,200 ft.) was estimated to be 11,138 ft^3 (315 m^3). This value is in reasonable agreement with estimated typical cuttings discharge of 334 m^3 from a 10,000 foot well (Shinn, 1974).

Rate of accumulation of waste effluents by the other solids control equipment in the drilling mud system (desander, desilter, centrifuge, sand trap, and sample trap; Figure 1, Table 10) will depend in large part on rate of drill cuttings production. Thus, rate of discharge from the total solids control system will decrease with time during the drilling operation (Figure 4; Ayers et al., 1980a). During the approximately five months required to drill an exploratory well to 4,970 meters (16,280 ft.) in NJ 18-3 Block 684 of the Mid-Atlantic outer continental shelf, approximately 268,800 gallons of solids control equipment effluents were discharged to the ocean. This effluent contained 863 metric tons of solids, 41 percent of which came from the shale shakers, 40 percent from the desander, and 19 percent from the mud cleaners. Most of this was drill cuttings. Perhaps 43 metric tons was drilling mud.

Whole used drilling mud is discharged intentionally in bulk quantities several times during drilling operations. Some mud may be discharged to make space in the mud tanks for addition of water or mud ingredients to change mud properties. If mud is pumped out of the hole for emplacement and cementing of casing, there may not be enough capacity in the mud tanks and the excess is discharged. Changeover of mud programs (e.g., from seawater lignosulfonate mud to freshwater lignosulfonate mud) may require bulk discharge of a large volume of mud. Volume of individual bulk mud discharges during normal drilling operations usually is in the range of 100 - 300 barrels (4,200 - 12,600 gal.) (Ray, 1979), but may exceed 2,000 barrels (84,000 gal.) for a major change of mud program. A single bulk discharge might last for 15 minutes to two hours. Bulk discharges may take place only a few times during drilling (Figure 3; Ray and Meek, 1980) or almost daily (Figure 5; Ayers et al., 1980a). More frequent bulk discharges are required if dilution is used to control solids build-up in the mud, as

Table 10. Summary of drilling mud discharges from an exploratory drilling platform in Lower Cook Inlet, Alaska. Volumes have been converted to gallons according to 1 barrel = 42 gallons (From Houghton et al., 1980).

Source or Type of Discharge	Volumetric Composition (%)	Discharge Frequency	Discharge Rate	Estimated Maximum Daily Discharge
Continuous discharges from:				
Shale Shakers	50% Cuttings 7.5% Drilling Mud Solids 42.5% Water	Continuous during drilling	42-84 gal/hr	1,008 - 2,016 gal
Desander	25% Sand 75% Water	2-3 hr/day during drilling	126 gal/hr	252 - 378 gal
Desilter	22.5% Silt 2.5% Drilling Mud Solids 75% Water	2-3 hr/day during drilling	672-714 gal/hr	1,344 - 2,142 gal
Centrifuge	1% Drilling Mud Solids 99% Water	1-3 hr/day as required	1,260 gal/hr	1,260 - 3,780 gal
Sand Trap	20% Sand 7.5% Drilling Mud Solids 72.5% Water	Every 2-3 days for 2-10 min[1]	4,000 gal in 2-10 min	4,000 gal
Sample Trap	15% Drilling Mud Solids and Cuttings 85% Water	Every 2-3 days for 5-10 min[1]	630 gal/hr	52.5 - 105 gal
Bulk Discharges from:				
Cementing	10-15% Drilling Mud Solids 85 - 90% Water	3-6 times per well[1]	420 gal/min for up to 20 min	8,400 gal
Dilution Rheology	10-15% Drilling Mud Solids 85 - 90% Water	Less than 3 per well[1]	29,400 gal/hr (max 8,400 gal)	8,400 gal
End of Drilling	10-15% Drilling Mud Solids 85 - 90% Water	Once per well[1]	29,400 gal/hr (up to 3 hr)	88,200 gal

[1] Not discharged during drilling.

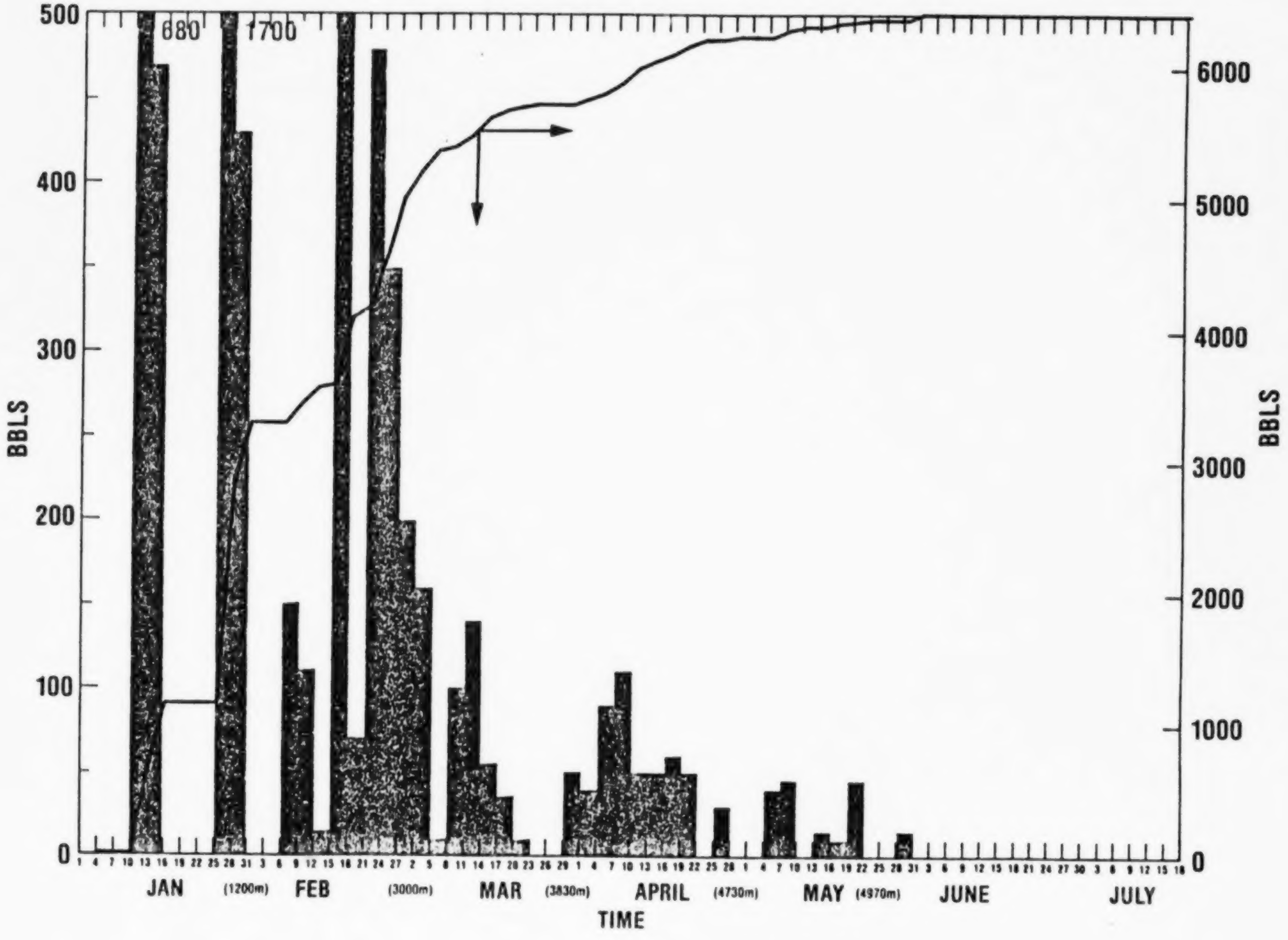


Figure 4. Daily and cumulative volume of solids control equipment discharges (mainly cuttings and water) during exploratory drilling in the Baltimore Canyon off New Jersey (From Ayers et al., 1980a).

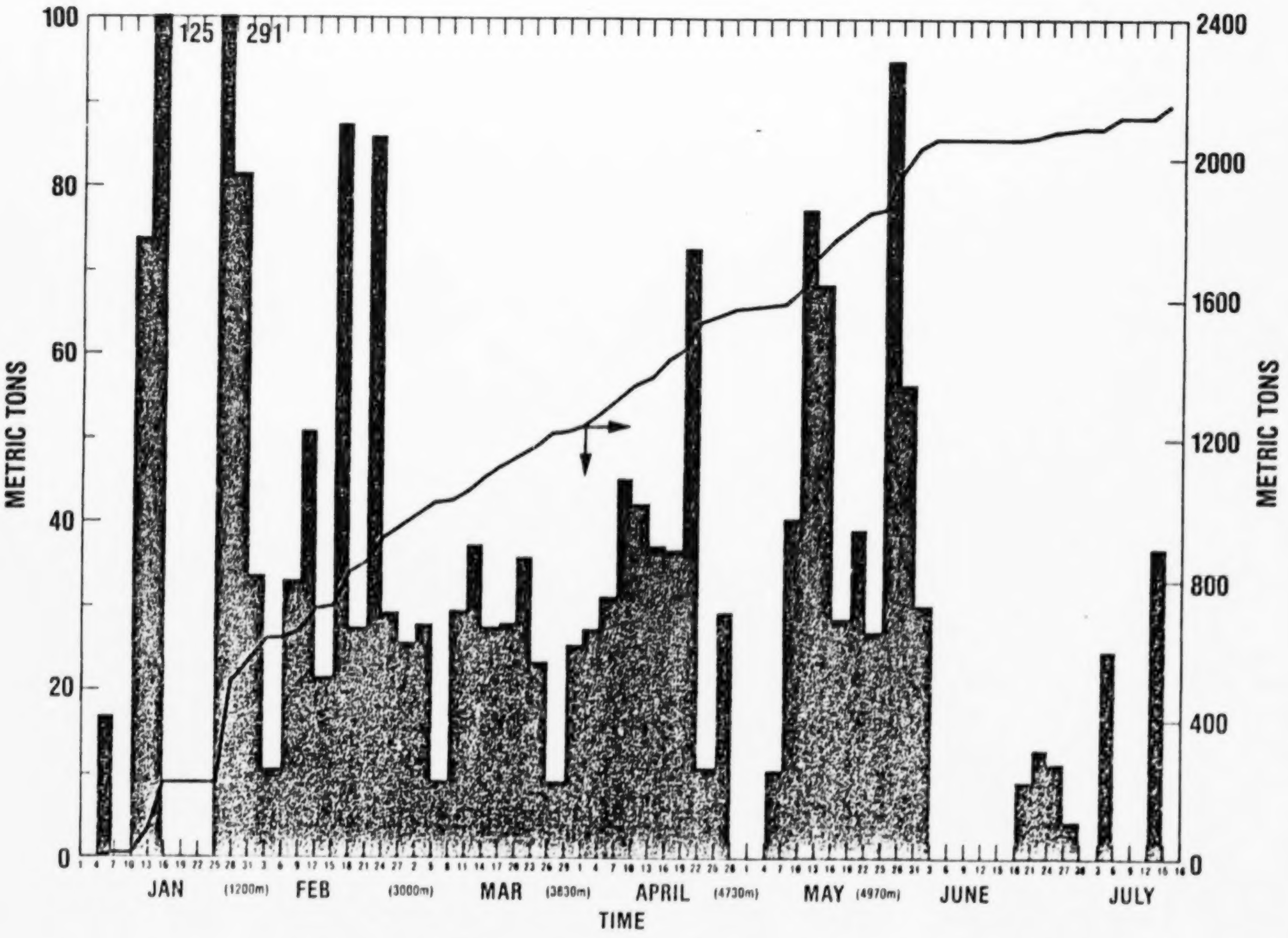


Figure 5. Daily and cumulative volume of total solids discharges (bulk mud discharges plus solids control equipment discharges) during exploratory drilling in the Baltimore Canyon off New Jersey (From Ayers et al., 1980a).

was the case in the Mid-Atlantic OCS exploratory program described by Ayers et al. (1980a).

At the end of the drilling operation, any drilling mud remaining in the mud system usually is discharged to the ocean. Volume of this bulk discharge will depend somewhat on volume of mud tanks and depth of hole (the hole may contain more mud that the mud tanks). It is usually in the range of 1,000 - 2,500 barrels (42,000 - 105,000 gal.) (Ray, 1979). Several bulk mud discharges may take place at the end of drilling, each lasting one to several hours (Figures 3 and 5).

In the two drilling operations discussed here, total volumes of mud discharged to the ocean during the entire drilling operations were 2,460 barrels (103,320 gal.: Tanner Bank; Ray and Meek, 1980) and 30,800 barrels (1,293,600 gal.: Mid-Atlantic OCS; Ayers et al., 1980a). In the latter study, total solids in the discharged drilling mud amounted to 1,287 metric tons. The values are fairly representative of the amounts of mud discharged during normal offshore drilling operations.

Design of mud and cuttings discharge systems varies from one rig to another (Ray, 1979). Discharge may be directly from the platform surface with free-fall to the water. A flexible hose may be rigged to carry the mud and cuttings to the water surface. Alternatively, shunt pipes 12 to 18 inches in diameter may be an integral part of the rig. The shunt pipe may discharge mud and cuttings anywhere from near the surface to just above the bottom. Some consideration should be given to designing a mud/cuttings shunt pipe system that would maximize dilution of effluents with ambient seawater before they are released to the ocean.

Dispersion and Dilution in the Water Column

Drilling mud is a slurry of solid particles of different sizes and densities in water. Various mud additives may be water-soluble, colloidal, or particulate. Clays, silt and cuttings have a specific gravity of about 2.6 g/cc, while barite has a specific gravity of about 4.2 - 4.5 g/cc. As a result of this physical/chemical heterogeneity, upon discharge to the ocean, drilling mud undergoes substantial and rapid fractionation. Drill mud discharged from a submerged discharge pipe can be thought of as going through three distinct phases: convective descent of the jet of material, dynamic collapse, and passive diffusion (Figure 6; Brandsma et al., 1980). In the jet phase, the plume descends rapidly, entraining low-density particles and bending toward the direction of current flow. Dynamic collapse begins when the plume encounters the level of neutral buoyancy or the sea bottom. Vertical descent is retarded. The plume flattens in the vertical axis and broadens in the horizontal axis. Lighter particles and soluble materials may begin to ascend, while heavier particles settle on the bottom. Even in the jet phase, the larger denser particles may leave the plume and descend at a more acute angle than the plume itself. The diffusion phase occurs when the kinetic energy imparted to the plume at discharge is used up and movement of the plume is controlled by convection and turbulence of the ambient medium and by simple diffusion and gravitational settling of the mud components. During this entire process, the mud plume is being diluted continuously with seawater and by settling to the bottom of denser fractions. Critical determinants of the impact of discharged drilling mud on the water column and its biota are the rate and extent of this dispersion/dilution process.

Several detailed investigations have been performed of rate of dispersion and dilution of drilling muds discharged at different rates from offshore platforms in the Atlantic, Pacific and Gulf of Mexico. Ray and Shinn (1975) observed that drilling mud and cuttings discharged at 35 feet below the surface from an oil rig in 245 feet of water in the Gulf of Mexico fractionated rapidly. Finer, low density particulates rose vertically, spread horizontally, and were dispersed down-current. Heavy and larger particulates fell almost straight down and accumulated on the bottom under the discharge pipe. Of several water-column parameters measured in an effort to quantify dispersion and dilution of the drilling mud plume, only total suspended solids showed elevated values near the discharge point. Elevated total suspended solids concentrations were detected about 90 feet east and west of the platform, but not at greater distances, during mud/cuttings discharge.

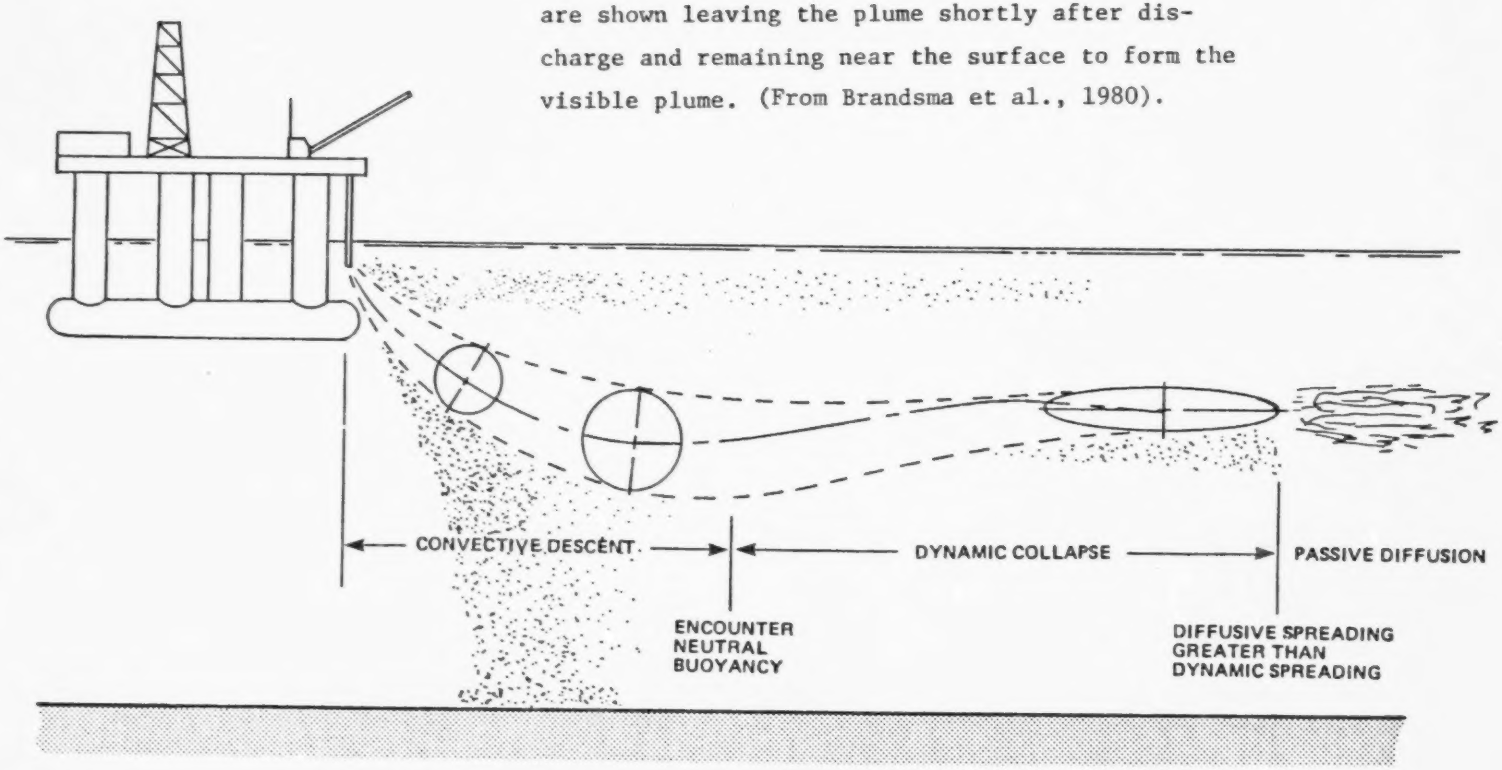

CONVECTIVE DESCENT
DYNAMIC COLLAPSE
PASSIVE DIFFUSION
ENCOUNTER NEUTRAL BUOYANCY
DIFFUSIVE SPREADING GREATER THAN DYNAMIC SPREADING

Figure 6. Idealized jet discharge described by mathematical model. Cross-sections are shown at three stages of the plume. A heavy class of particles is depicted settling out of the plume at an early stage. Lighter particles are shown settling during the collapse phase. Very fine particles are shown leaving the plume shortly after discharge and remaining near the surface to form the visible plume. (From Brandsma et al., 1980).

Zingula (1975) obtained roughly similar results in an investigation of drilling mud discharges from a platform in Timbalier Bay, Louisiana. Total suspended solids concentrations reached background values 660 feet down-current from the discharge pipe. At 300 feet, total suspended solids concentration was 40 mg/l compared to a background concentration of about 5 mg/l. Drilling mud/cuttings collected directly below the shale shaker had a total suspended solids concentration of about 350,000 mg/l, while water at the exit of the discharge pipe had a total suspended solids concentration of 278 mg/l. This indicates that drilling mud may be diluted approximately 1,000-fold in the discharge pipe before actual discharge to the ocean.

A detailed drilling mud and cuttings monitoring study was performed during exploratory drilling from a semi-submersible drilling platform on Tanner Bank in the Pacific Ocean 161 km west of Los Angeles, California (Ecomar, 1978; Ray and Meek, 1980). Physical and chemical characteristics of mud plumes were monitored during several normal mud discharges (Table 11).

Discharges A and B were at a rate of 10 bbl/hr (420/gal/hr) into seawater moving at a speed of 11.8 and 45.2 cm/sec, respectively. The nearly four-fold difference in current speed had little effect on rate of plume dilution as measured by any of several physical or chemical parameters. As expected, there was a tendency for near-field dilution to be more rapid under high than under low current speeds. In both cases, however, initial dilutions were extremely high within 3 m of the discharge pipe, ranging from 500:1 to almost 1,000:1. These initial dilution rates are based on a measured suspended solids concentration of 250,000 mg/l in the drilling mud entering the discharge pipe on the platform. Total suspended solids concentrations approached background values within about 200 m of the discharge. Particulate heavy metals concentrations in the plumes approached background within 150 m of the discharge.

In discharge D, initial dilution in the discharge pipe (250,000 mg/l to 43.04 mg/l) was even greater than in the earlier studies. Suspended solids concentration had reached background by 90 meters down-current. The heterogeneous nature of drilling mud plumes is indicated by the manner in

Table 11. Summary of drilling mud discharge plume data from several metered drilling mud discharges from an exploratory drilling platform on Tanner Bank off Southern California. Heavy metals concentrations are for the solid phase alone (From Ray and Meek, 1980).

Discharge Rate	Station	Distance(M)[1]	Depth(M)[2]	Current Speed (cm/sec)	Transmittance(%)	Suspended Solids (mg/l)	Barium (μg/l)	Chromium (μg/l)	Lead (μg/l)
10 bbl/hr	A1	0	12	11.8	-	499	23,560	824	38
	A2	105	12		49.1	5.20	103	4.07	0.395
	A3	155	8		62.8	2.03	46.6	0.859	0.398
	A4	450	23		77.1	1.79	37.8	0.865	0.477
	A-Control	91	15		83.4	1.54	13.5	0.430	0.373
10 bbl/hr	B1	0	12	45.2	-	252	7,780	346	17.6
	B2	76	15		66.7	1.95	22.2	1.44	0.490
	B3	145	15		65.7	1.17	34.3	0.928	0.232
	B4	440	5		48.4	1.01	38.3	0.707	0.325
	B-Control	76	15		82.0	0.829	62.3	0.443	0.429
12 bbl/hr	D1	0	12	29.8	-	43.04	1,033	43.50	263
	D2	90	10		46.0	1.59	67.6	1.90	0.424
	D3	130	15		51.6	2.20	112	2.31	0.404
	D4	175	15		74.6	2.11	52	2.23	1.011
	D5	250	20		77.5	1.33	17.1	1.01	0.211
	D6	350	10		83.3	1.51	21.8	1.09	0.194
20 bbl/hr	E1	0	12	2.2	-	279	3,860	238	5.03
	E2	55	10		28.4	2.74	75.5	1.97	0.249
	E3	140	5		41.3	1.81	39.5	1.07	0.337
	E4	200	10		40.5	2.18	49.3	2.42	0.298
	E5	275	15		63.4	1.01	26	0.534	0.237
	E6	310	5		55.6	1.56	35.6	1.62	0.400
754 bbl/hr	G1	0	12	15.9	-	328	12,700	917	40.5
	G2	74	10		0.0	25.2	575	13.5	2.74
	G3	500	5		19.3	4.04	146	16.4	0.880
	G4	625	20		80.8	1.10	47.2	0.528	0.455
	G5	800	20		23.7	4.73	111	7.37	4.4
	G6	1,000	25		10.9	0.563	26.2	0.916	0.116
	G-Control	373	15		94.8	0.814	21.9	0.481	0.223

1. Meters down stream from the discharge; 2. Depth is point of maximum plume density (determined by transmissometry where samples were taken).

which values for water quality parameters fluctuate up and down with distance from the discharge.

When rate of drilling mud discharge was increased to 20 bbl/hr (840 gal/hr), there was little change in the rate of mud dilution. Background concentrations of total suspended solids were approached within 55-140 m of the discharge pipe. Rate of heavy metal dilution was similar to that of suspended solids.

Drilling mud dilution and dispersion were much less rapid during a high rate mud discharge of 754 bbl/hr (31,668 gal/hr). Background concentrations of total suspended solids were not approached until 800-1,000 m from the discharge. Particulate heavy metals also reached background at about 1,000 m.

Transmissometry values (% transmittance) tended to return to normal control or background values more slowly than other water column parameters used to monitor drilling mud dilution. Percent transmittance, a measure of the transparency of water, is perhaps the best measure of the dilution of the very fine clay-sized particulate fraction of the mud and cuttings. During low-rate discharges, percent transmittance approached background within 275-450 meters of the discharge in most cases. During the high rate mud discharge, percent transmittance was still very low 1,000 m from the discharge. The results suggest that mixing and dilution of the very fine clay-size particulate fraction of mud and cuttings is slower than dilution of coarser, denser fractions, the latter containing most of the particulate metals of concern.

Rapid dilution of drill mud in the discharge pipe before the mud exited to the ocean was attributed to oscillatory in-and out-flux of water in the vertically-mounted discharge pipe due to wave action.

Ayers et al. (1980b) studied dilution and fate of two experimental discharges of a typical chrome lignosulfonate-clay mud (bulk density 17.4 lb/gal) from an exploratory rig in 23 meters of water in the Gulf of Mexico. In the first, 250 barrels of mud were discharged at a rate of 275 bbl/hr

(11,550 gal/hr). In the second, 389 barrels of mud were discharged at a rate of 1,000 bbl/hr (42,000 gal/hr). These high discharge rates were typical of those used at the end of a drilling operation to empty the mud tanks before moving the platform to a new location.

During both discharges, the mud formed two plumes. The lower plume, containing most of the discharged material and especially the denser, coarser particulate fractions, descended quickly to the sea floor. As the lower plume descended, an upper, near surface plume was generated by turbulent mixing of the lower plume with seawater. The upper plume, containing much of the fine clay-sized low density particulates, persisted longer in the water column than the lower plume, and was carried away from the discharge by water currents.

During both discharges, total suspended solids concentrations declined very rapidly with distance from the discharge (Table 12). During the 250 bbl/hr discharge, suspended solids concentration reached background within about 364 meters of the discharge. In the 1,000 bbl/hr discharge, the background concentration of suspended solids was reached in about 878 meters.

Percent transmittance values rose slowly with distance from the discharge. Background values for percent transmittance were reached at 625 and 1,470 meters during the 250 and 1,000 bbl/hr discharged, respectively. Again, this indicates the slower rate of dilution and dispersion of fine clay-sized particulates than coarser particles in the water column. While both fine and coarse particulates contribute to both total suspended solids concentration and percent transmittance values, the coarser particles make up the bulk of the weight of suspended solids, while the finer particles contribute more than the coarser particles to the decrease in water transparency.

Drilling mud plumes become progressively more dilute as they are transported away from the discharge point by water currents. A quantitative parameter extremely useful in assessing potential environmental impacts of drilling mud plumes is time required for water quality parameters in the plume to reach background values. If values for these parameters are plotted graphically versus transport time (distance from discharge point

Table 12. Dilution and dispersion of two drilling mud plumes produced by high rate high volume discharges of used chrome lignosulfonate drilling mud from an offshore exploratory platform in the Gulf of Mexico (From Ayers et al., 1980b).

Discharge Rate	Distance From Source (Meters)	Depth (Meters)[1]	Suspended Solids (mg/l)	Transmittance(%)
275 bbl/hr (250 bbl discharged)	0 (Whole Mud)	-	1,430,000	-
	6	8	14,800	-
	45	11	34	2
	138	9	8.5	56
	250	9	7.0	48
	364	9	1.2	37
	625	9	0.9	71
	Background		0.3-1.9	76-85
1,000 bbl hr	0 (Whole Mud)	-	1,430,000	-
	45	11	855	0
	51	12	727	0
	152	11	50.5	2
	375	16	24.1	4
	498	14	8.6	23
	777	13	4.1	21
	878	2	1.2	71
	957	12	0.83	76
	1,470	11	2.2	82
	1,550	9	1.1	82
	Background		0.4-1.1	80-87

[1] Depth at which highest plume concentration was found.

divided by current speed), a curve asymptotically approaching the background value is obtained. This curve defines the rate of dilution or change of the water quality parameter. Rates of dilution of total barium, aluminum and chromium during the two mud discharges described by Ayers et al. (1980b) are summarized in Figures 7, 8 and 9. During the 250 bbl/hr discharge, barium, aluminum (a tracer for the clay fraction), and chromium reached background values in about 70 minutes, 30 - 50 minutes, and 20 - 55 minutes, respectively. Dilution of the metals to background concentrations in the water column took longer during the 1,000 bbl/hr discharge. Times required were about 110 minutes, 90 - 110 minutes, and 90 - 100 minutes for barium, aluminum and chromium, respectively. Relationship between rate of drilling mud discharge and rate of dilution to background is depicted graphically in Figure 10.

This study shows that during high rate discharge of drilling muds to the ocean, dilution of mud solids to background concentrations occurs within about 1,000 meters down-current from the discharge point and is accomplished in less than two hours.

Somewhat similar results were obtained during an investigation around an offshore rig in the Mid-Atlantic outer continental shelf about 156 km east of Atlantic City, New Jersey in 120 meters of water (Ayers et al., 1980a). During a 500 bbl/hr discharge, the lower, rapidly descending plume containing the bulk of the discharge contained 1,195 mg/ℓ total suspended solids 15 meters down-current from the discharge in 24 meters of water. The upper plume was much more dilute. In the upper plume, background concentrations of suspended solids were reached at about 350 meters during a 500 bbl/hr mud discharge and at 600 meters during a 275 bbl/hr discharge. During the 500 bbl/hr test, the plume flattened noticeably near the surface and was not detectable below about five meters depth within 150 meters down-current from the discharge. During the 275 bbl/hr test, the plume center remained ten to fifteen meters deep for a distance of about 600 meters from the discharge. As in the Gulf of Mexico study, values for percent transmittance reached background at a greater distance from the discharge than the distance at which suspended solids concentration reached background.

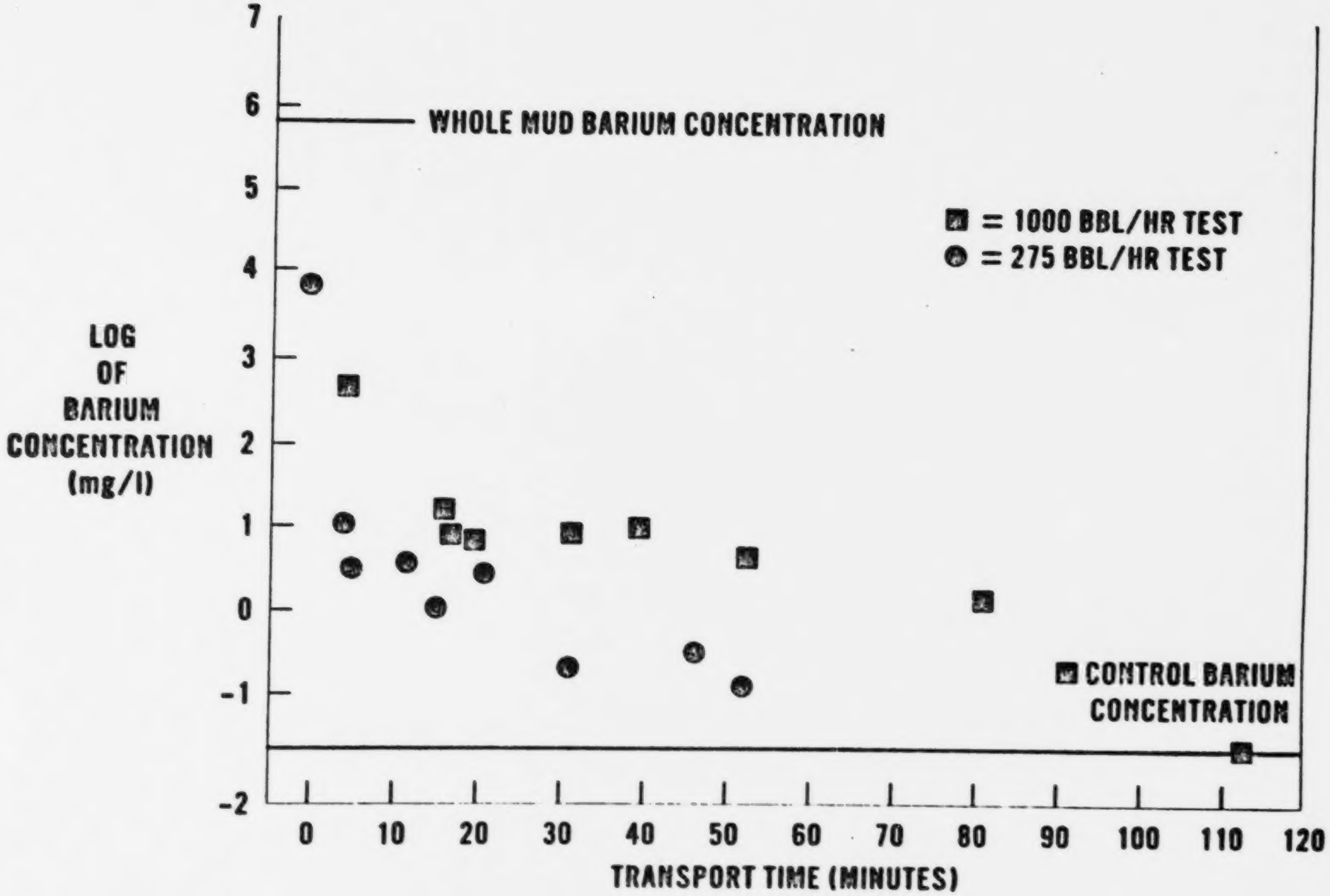


Figure 7. Decline in maximum total barium concentration in drilling mud plumes with transport time (distance from discharge/current speed) during two high-rate bulk drilling mud discharges (From Ayers et al., 1980b).

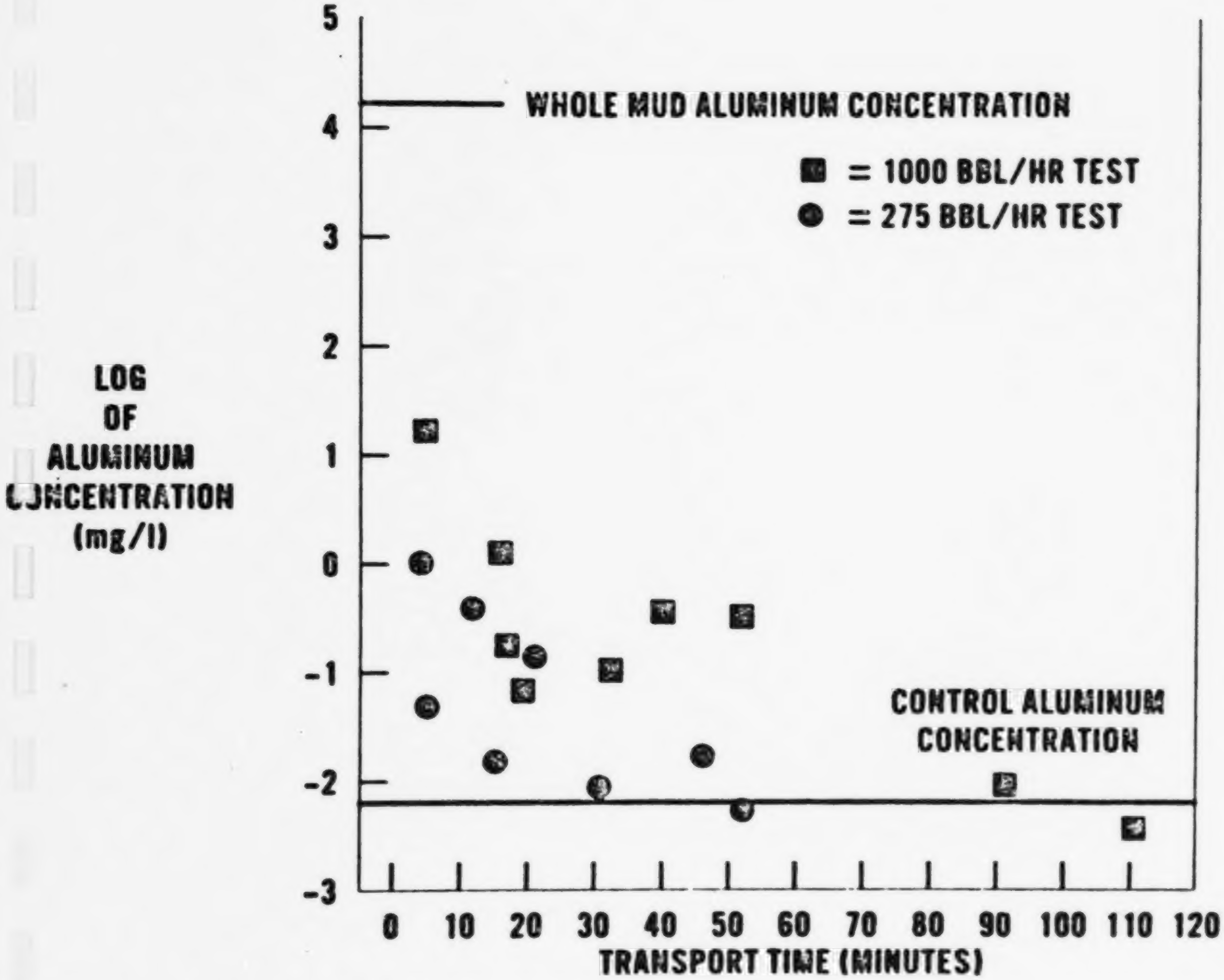


Figure 8. Decline in maximum total aluminum concentration (a marker of the clay fraction) in drilling mud plumes with transport time during two high-rate bulk drilling mud discharges (From Ayers et al., 1980b).

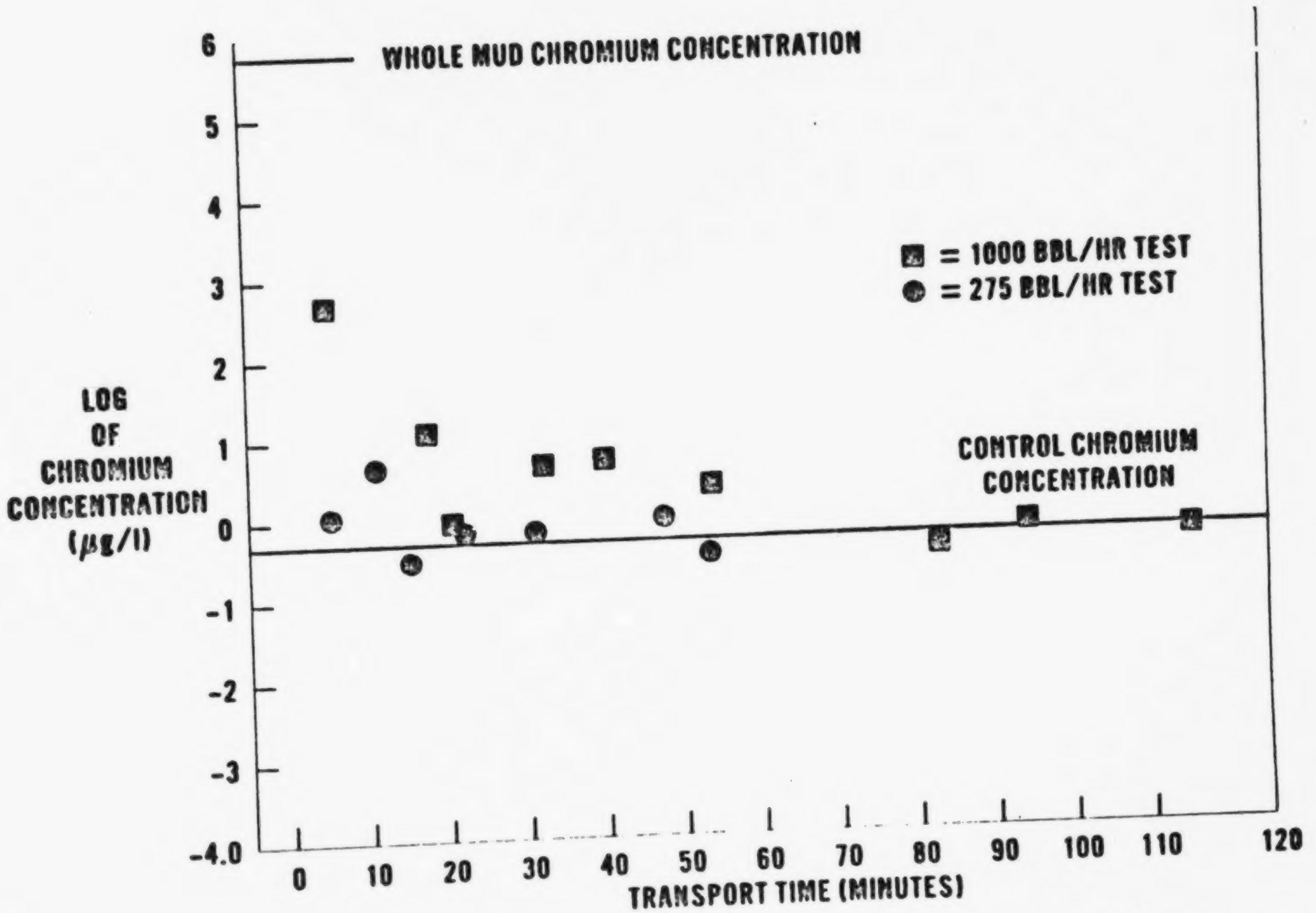


Figure 9. Decline in maximum total chromium concentration in drilling mud plumes with transport time during two high-rate bulk drilling mud discharges (From Ayers et al., 1980b).

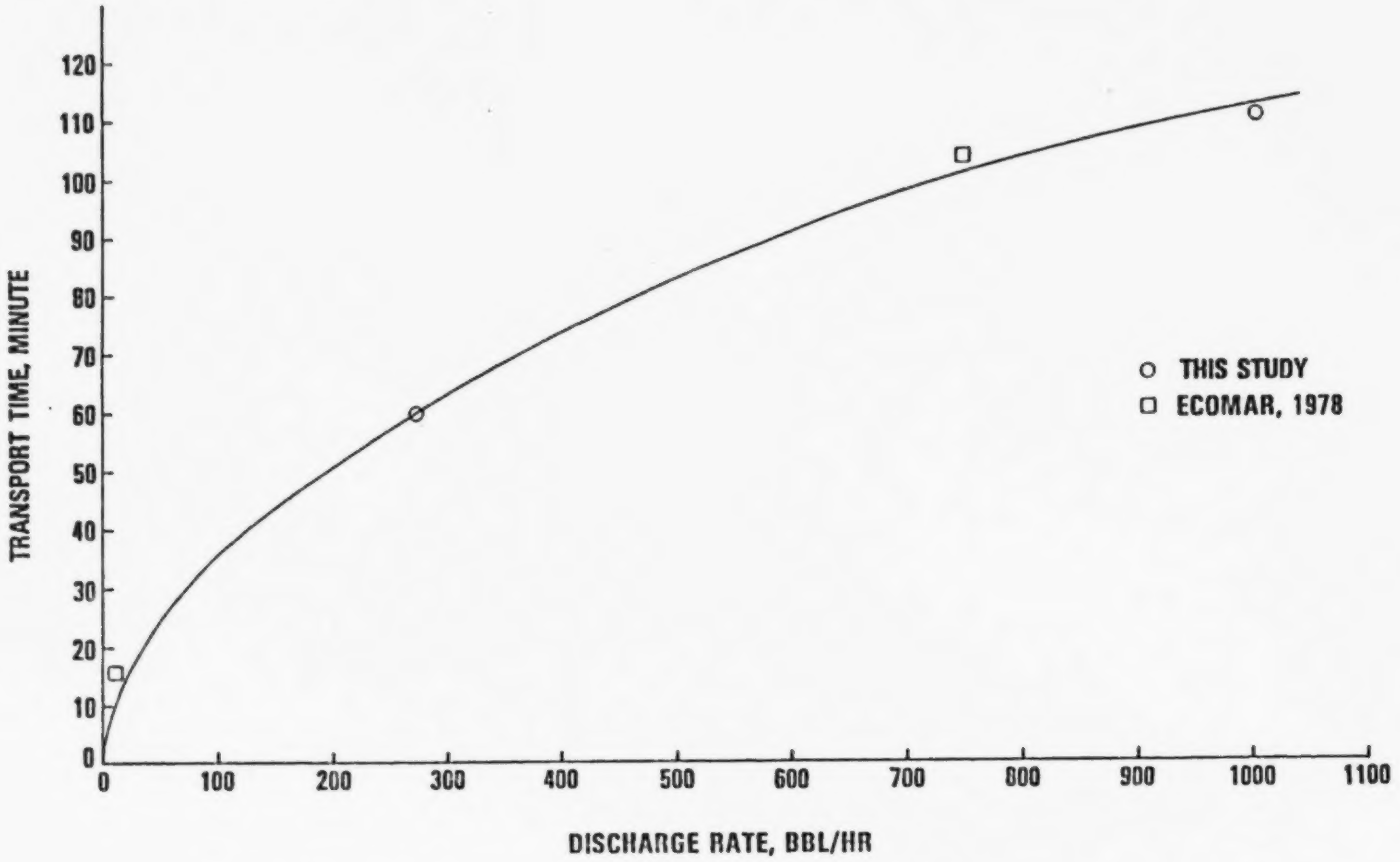


Figure 10. Relationship between bulk drilling mud discharge rate and transport time (distance from discharge/current speed) required for solids concentration in the drilling mud plume to reach background (From Ayers et al., 1980b).

Houghton et al. (1980b) measured dilution and dispersion of two small and one continuous discharge of mud and cuttings from a semi-submersible drilling vessel in Cook Inlet, Alaska. Dye dilution, using Rhodamine WT, and transmissometry were used to track the plume. Turbulence created by the strong water currents moving around the drilling vessel caused very rapid dilution of the drilling mud plume. In the two small bulk discharges, a dilution of 2.2 X 10^4 was observed about 800 meters down-current from the discharge. The plume did not descend deeper than about 23 meters.

During the continuous mud discharge also, the mud plume did not descend deeper than 23 - 30 meters. The dye was diluted more than 10^4-fold within 100 meters and within a few minutes of the discharge. These rapid dilutions were caused by the convective mixing resulting from the fast-moving and complex three dimensional flow-field created by the hull of the drilling vessel.

During discharge of used drilling mud as a heavy spray to the surface of the ocean from a drilling rig in the Gulf of Mexico, suspended solids concentration in the surface water was about 10-fold above background about 200 m down-current from the rig (Trocine et al., 1981; Trefry et al., 1981). Estimated dilution of drilling mud at this point was 0.5 x 10^6-fold compared to solids concentration of whole drilling mud. A rapidly moving surface current above a distinct pycnocline restricted vertical advection of the plume somewhat. Thirteen hours after termination of the discharge, total suspended solids concentrations had increased to well above background below the pycnocline at a station 800 meters from the rig (from about 100 to about 200 ug/1 suspended solids). Sixteen hours after the discharge, at a distance of 3.2 km from the rig, the particulates were concentrated in a 15 meter thick nephloid layer just above the bottom. The nephloid layer was composed primarily by resuspended sediments.

Concentrations of particulate metals, chromium, iron, and barium, showed a temporal/spatial distribution similar to that of suspended solids concentration. Barium penetrated the pycnocline into deeper water most rapidly, followed by iron, then chromium. This reflects the differences in density of the particles with which these metals were associated.

Background concentrations of particulate Cr, Ba and Fe in the ocean near the rig site were less than 4, 30, and 200 ng/l, respectively. One km down-current from the rig, ten hours after termination of the discharge, particulate chromium concentrations were from 1 to 11 ng/l. Particulate matter iron concentrations were about 100 ng/l in the surface waters, and rose to 1,800 ng/l 10 meters above the bottom due to the presence of a nephloid layer composed of resuspended sediment. Particulate barium concentrations were uniform throughout the water column at 80 ng/l, somewhat elevated above the 30 ng/l background values. Thus, using highly refined and sensitive analytical techniques, the authors were able to detect remnants of the mud plume 10 hours after and 1 km away from the discharge. These investigations also demonstrated the usefulness of particulate barium as a tracer of drilling mud plumes.

The investigations reviewed above are all in reasonable agreement in showing that drilling fluids discharged to the oceans are diluted and dispersed very rapidly, both spatially and temporally. Several thousand-fold dilutions are nearly always encountered within a few hundred meters down-current of the discharge pipe. Background conditions (depending on the water quality parameters measured and sensitivity of analytical technique) are usually approached within one-thousand meters of the discharge, though traces of the discharge can still be detected by the most sensitive techniques.

Because of the intermittent nature and variable rate of drilling mud and cuttings discharges from offshore platforms, and the rapid dilution of discharged drilling mud, it is apparent that drilling mud concentration in the water column, with respect either to a moving water mass or a geographic point, will never remain high for a long period of time.

Deposition of Drilling Muds in Bottom Sediments

Virtually all the solids and some of the soluble components (through adsorption to particulates) of drilling muds eventually are deposited in bottom sediments adjacent to and down-current from the drilling platform. Points of concern about such deposition are that mud and cuttings may accumulate on the bottom to depths that would physically smother benthic epi- and infaunal organisms, that such deposition might change sediment texture or chemistry, rendering the substrate unsuitable for certain species of marine organisms, that metals and other potentially toxic mud ingredients might accumulate in sediments, either killing benthic organisms or serving as a source of contamination of marine food webs. As a result of these concerns, much research has been performed in recent years on the deposition and accumulation of drilling muds and, in particular, mud-associated metals in sediments around drilling platforms.

Exploratory drilling activities around the Flower Gardens Banks, a coral reef system in the Gulf of Mexico off the Texas coast, have been the subject of several monitoring studies. To protect these unique coral reefs, several stipulations were made in permits, including that drill mud and cuttings be disposed of by shunting through a downpipe that terminates approximately 10 meters above the bottom for all drilling within three miles of the banks, and that no drilling be allowed within one mile of the banks (Gettleson, 1978). During and after drilling of an exploratory well near the East Flower Garden Bank, there was a significant increase, compared to pre-drilling values, in concentration of barium, iron and lead in sediments at the drill site (Continental Shelf Associates, 1975). Barium concentration increased from 22 to 425 mg per kg (ppm); iron concentration increased from 8.3 to 13,000 ppm; and lead concentration increased from 4.6 to 12.7 ppm. There was no change in sediment hydrocarbon concentration due to drilling. Because the drilling mud/cuttings outfall was located near the bottom, elevated metals concentrations in sediments were restricted to a small area near the discharge site.

In an investigation around another exploratory well nearby, mean barium concentrations in sediments decreased with distance from the discharge pipe after drilling (Continental Shelf Associates, 1976; Gettleson, 1978). Mean sediment barium concentration at the drill site before drilling was 560 ppm. After drilling, sediment mean barium concentrations were 2,924, 1,953, 1,750 and 989 ppm for circles around the drill site with radii of 100, 300, 500, and 1,000 meters. No excess barium was detected in the coral reef zone after drilling (barium concentrations 12.4 - 16.8 ppm). Based on these results, Gettleson (1978) estimated that approximately 50 percent of the drilling mud barium discharged was deposited within 1,200 meters of the discharge point.

In reviewing results of investigations of distribution of drilling mud-derived barium around five exploratory drill sites in the Gulf of Mexico, Gettleson and Laird (1980) concluded that the distance from the rig to which barium is dispersed and its concentration in bottom sediments depends on types and quantities of mud discharged, hydrographic conditions at the time of discharge and height above the bottom at which discharges are made. There were large differences in the distribution of barium in sediments around and down-current from the five wells after drilling was completed (Figure 11). Some trends do emerge however. In the examples included in Figure 11, sediment barium concentration was higher 100 meters down-current from the discharge than immediately under the discharge pipe, indicating that even when muds are shunted to near the bottom, some down-current drift takes place. Bottom currents in the vicinity of these wells were generally less than 8 cm/sec. In all cases, sediment barium concentrations were approaching background within 1,000 meters of the discharge. There was a tendency for some of the barium in drilling mud discharged at or near the surface (Figure 11, Block 367) to be transported further down-current before deposition than barium in drilling mud discharged near the bottom. This was not consistent, however.

Barium was used as a drilling mud tracer because of its extremely high concentrations in the muds being discharged (the muds were 87 - 90 percent barite by weight) (Gettleson and Laird, 1980). Other metals associated with drilling muds showed much less enrichment in sediments when any enrichment at all could be demonstrated. For instance, in another study of drilling mud dispersion from an exploratory rig in the northwest Gulf of Mexico, Trocine et al. (1981) reported elevated post-drilling levels of sediment barium as high as 5,200 ppm in the upper one centimeter of sediment at stations nearest the rig. Sediment barium concentration dropped to background level at the 5 cm depth in the sediment. Surficial sediments 1.9 km down-current from the discharge contained a three-fold above background barium concentration. These data show that metal enrichment of sediments from discharged drilling mud is restricted to the surficial layer of sediment.

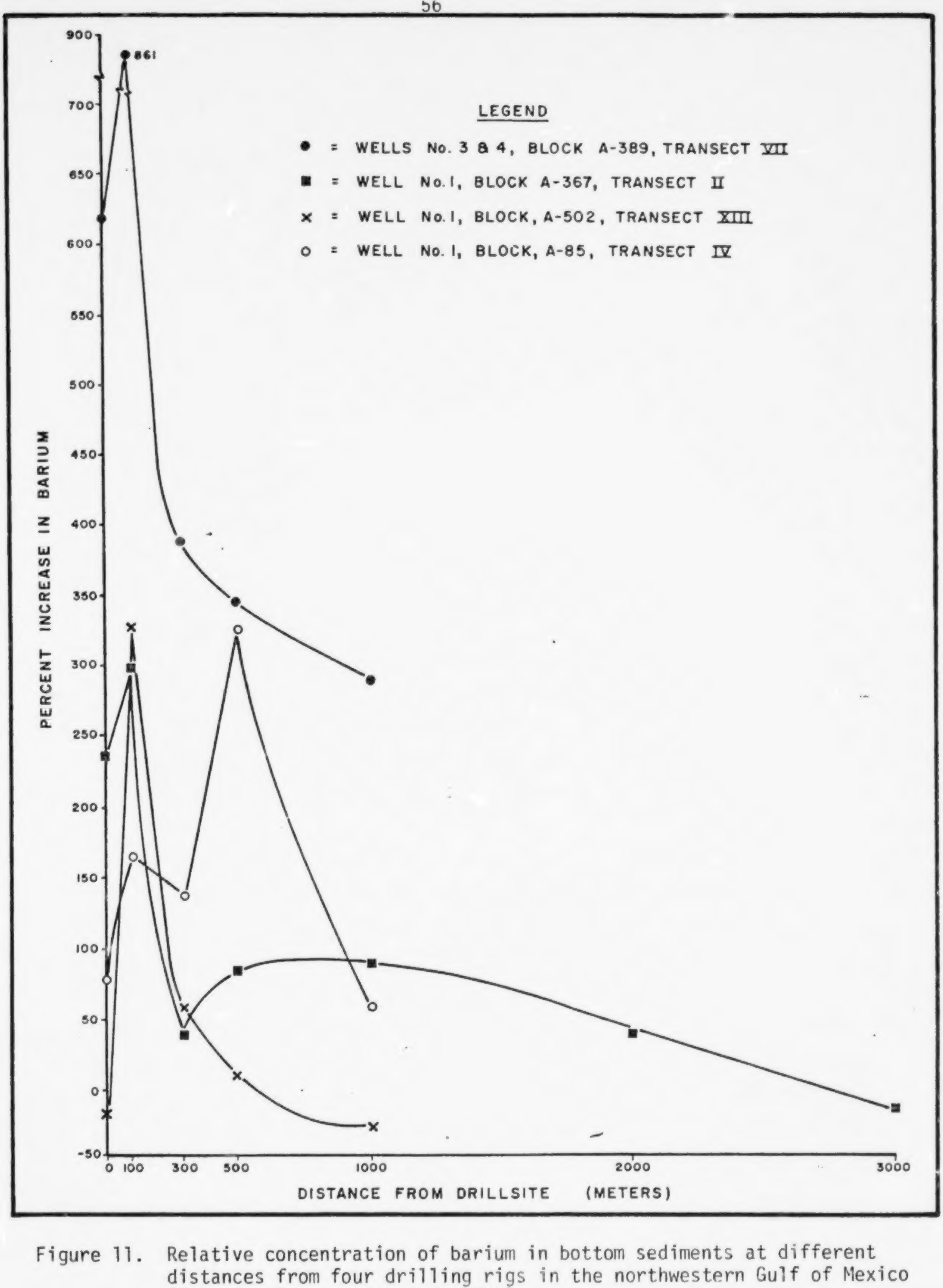


Figure 11. Relative concentration of barium in bottom sediments at different distances from four drilling rigs in the northwestern Gulf of Mexico (From Gettleson and Laird, 1980).

Enrichment of iron in the sediments was found only at stations closest to the rig. Chromium concentrations did not deviate significantly from normal at any station.

Following an exploratory drilling operation on the Atlantic outer continental shelf off Jacksonville, Florida during which 23,863 barrels (1,002,246 gal.) of drilling mud and 1,508 barrels (63,336 gal.) of cuttings were discharged, no increase in concentration of barium or chromium could be detected at any station around the rig (EG&G, 1980). Sediment traps collected particulates containing elevated levels of barium and chromium. The authors concluded that most of the discharged drilling muds must have been carried out of the study area by bottom currents.

Slightly different results were obtained around an exploratory platform on the Tanner Bank off Los Angeles, California. During the 85-day study period, 2,854 barrels (119,868 gal.) of mud and cuttings containing 863,290 kg of solids were discharged. Current speeds in the area averaged 21 cm/sec (Ecomar, 1978; Meek and Ray, 1980). Based on sediment trap data, the authors estimated that 12 percent of the total solids discharged settled out in the area between the 50 and 150 meter radii from the platform. A majority of the remainder of the discharged solids settled initially within a 50 meter radius of the platform. However, little or no visible accumulation of drilling mud and cuttings was observed in this area, so most of the material (estimated between 44 and 94 percent) was transported out of the area by strong bottom currents.

There were slight increases in post-drilling compared to pre-drilling sediment samples in concentrations of barium, chromium and lead. Pre-drilling levels of barium ranged from 87 to 156 ppm and rose to 124 to 1,680 ppm in post-drilling samples. Sediment chromium concentrations rose from less than 0.7 ppm before drilling to 0.5 to 6.11 ppm after drilling. The range of sediment lead concentrations before drilling was 0.2 to 1.8 ppm and rose in post-drilling samples to 0.25 to 9.90 ppm.

Mariani et al. (1980) studied changes due to drilling mud and cuttings discharge in physical and chemical properties of sediments around the site of an exploratory drilling operation on the Atlantic outer continental shelf off New Jersey. Drilling discharges caused some localized changes in sediment grain size distribution and clay mineralogy. There was a slight decrease in percent gravel and sand and slight increase in percent silt and clay in post-drilling compared to pre-drilling sediment samples. Interestingly, percent montmorillonite clay in the sediment decreased from 14.45 - 26.90 percent in pre-drilling sediment samples to 10.2 - 18.1 percent in post-drilling samples. Percent illite, chlorite and kaolinite increased in post-drilling samples compared to pre-drilling samples. Because the mud used in this operation contained 24 - 38 percent montmorillonite by weight and much smaller amounts of the other clay types, while cuttings contained significant amounts of illite and kaolinite (Ayers et al., 1980a), it is likely that the change in clay mineralogy in sediments was due primarily to accumulation of drill cuttings. These changes in the clay fraction of the sediments extended out approximately 800 meters from the rig.

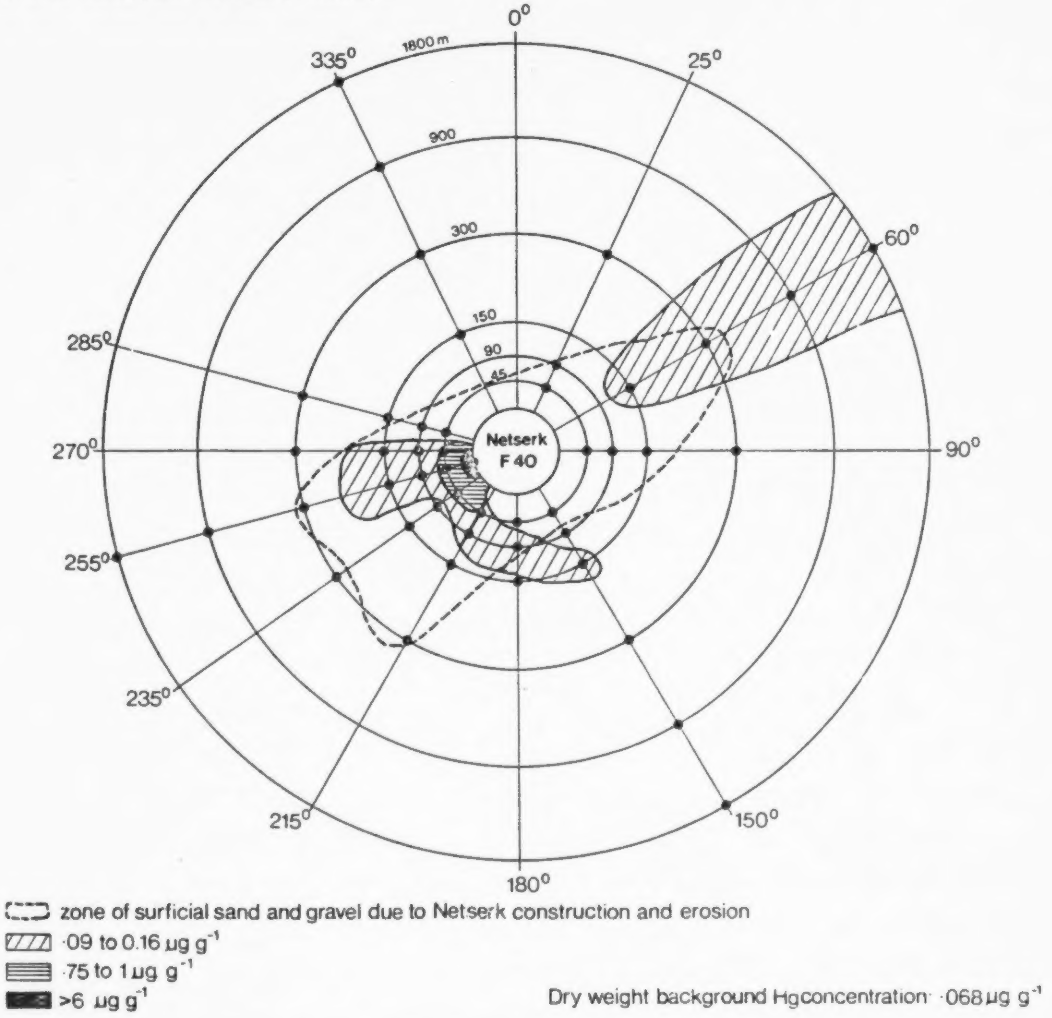
Sediment samples collected before and after drilling were analyzed, using a weak acid leachable atomic absorption spectrometry method for several metals (arsenic, barium, cadmium, chromium, copper, mercury, nickel, lead, vanadium, and zinc). Concentrations in sediments of only lead, barium, nickel, vanadium and zinc were higher in the post-drilling than in the pre-drilling survey. Increases in lead and zinc concentrations were small and were within the normal concentration range for these metals in sediments from the general area. Nickel and vanadium were not present in the mud and cuttings in significant concentrations, and so probably came from another source. Increases in sediment barium concentration were small. However, the weak acid extraction method (designed to extract potentially bioavailable metals) is a poor method for solubilizing barium and other metals from barite. Subsequent analyses by Mariani (personal communication) of archived pre- and post-drilling sediment samples for total barium by neutron activation analysis revealed significant differences between pre- and post-drilling sediment total barium concentrations. Sediment total barium concentrations before drilling started ranged from 147.0 to 276.28 ppm. In post-drilling sediment samples, total barium concentration ranged from 192.39 to 3,477.18 ppm. The highest concentration was from a sediment sample collected approximately 100 meters southwest of the drill site. Sediments at the drill site contained 159.33 ppm total barium before drilling and 1075.38 ppm after drilling. Post-drilling sediment samples west and south-southwest of the drill site contained 192.4 and 294.7 ppm barium, respectively, close to the normal range for pre-drilling sediment samples.

Crippen et al.(1980) studied distribution and concentration of mercury, lead, zinc, cadmium, arsenic, and chromium in surficial sediments around the Netserk F-40 well in the Beaufort Sea. During drilling of this well, approximately 7,300 barrels (306,600 gal.) of mud and cuttings were discharged to the ocean. The barite used to formulate these muds contained high concentrations of mercury, lead, zinc, cadmium, and arsenic (Table 7). All these metals were present in one or more sediment samples in the vicinity of the discharge site, especially within 45 meters of the discharge, at concentrations significantly higher than background. The mean background concentration of mercury in sediments from the region was 0.07 ppm. Mercury concentrations as high as 6.4 ppm were detected within 45 meters to the southwest of the discharge site (Figure 12). Between 90 and 220 meters to the southwest and west of the discharge site, sediment mercury concentrations ranged from 0.16 to 1.0 ppm. Elevated mercury concentrations were also observed in a transect to the northeast on the opposite side of the artifical island from the discharge to a distance of about 1,800 meters. Distribution in sediments around the discharge site of cadmium, chromium, lead and zinc was similar to that of mercury. Highest concentrations of these metals were recorded at the station closest to the discharge, where the sediment sample contained visibly identifiable drilling mud. Concentrations in this sample of arsenic, cadmium, chromium, lead, and zinc were 23.0, 5.9, 70.0, 467, and 1,360 ppm, respectively, all above background values.

Sediments in the vicinity of the Buccaneer oil and gas field, drilled in the early 1960's off Galveston, Texas, contain elevated levels of barium, cadmium, and strontium (Wheeler et al., 1980). Mean barium concentration in sediments near platforms was 403 ppm compared to 151 ppm in nearby control areas. The authors suggested that elevated barium and strontonium could have come from brines discharged from the production platforms, but did not provide data on the concentration of these elements in the brine. The

Distribution of Mercury in the surficial Netserk sediments **Figure 12.**

(From Crippen et al., 1980).


0°
25°
60°
90°
150°
180°
215°
235°
255°
270°
285°
335°
1800 m
900
300
150
90
45
Netserk
F 40
zone of surficial sand and gravel due to Netserk construction and erosion
·09 to 0.16 µg g-1
·75 to 1 µg g-1
>6 µg g-1
Dry weight background Hg concentration ·068 µg g-1

brines are enriched in these alkaline earth metals compared to seawater. Much of the barium and some of the strontium (a normal contaminant of barites) also were probably derived from drilling muds discharged 10 to 15 years earlier during drilling of the field. Cadmium probably came from corrosion of rig structures. Elevation of mean sediment cadmium concentration was not large (1.1 ppm versus 0.8 ppm for control). All other metals analyzed (cobalt, chromium, copper, iron, manganese, nickel, lead and zinc) had similar concentrations in the oil field sediments and in sediments from control areas.

Tillery and Thomas (1980) measured metal concentrations in sediments around several long-established production platforms in the Gulf of Mexico off Louisiana. Aluminum, calcium, cadmium. chromium, copper, iron, nickel, lead, vanadium, and zinc were analyzed in sediment samples collected 100, 500, 1,000, and 2,000 meters down-current from four production platforms and compared to values for control sediment samples. Gradients were observed of decreasing concentration in surficial sediments with distance from some platforms of barium, cadmium, chromium, copper, lead, and zinc. Concentration ranges in the gradients were not large and concentrations of these metals in sediments 100 meters from production platforms were only slightly higher than control values. These sediment metal gradients were attributed by the authors to discharged drilling fluids and cuttings, discharged produced waters, metallic debris on the bottom, pipelines, platform-related activities, or recreational boating.

All these investigations demonstrate that metals associated with drilling muds, especially barium, tend to accumulate in surficial bottom sediments near the rig when drilling fluids and cuttings are discharged to the ocean. Barium, because of its high concentration in most drilling muds, its extreme insolubility as barite, and its high density, is the drilling mud metal enriched to the greatest extent in sediments down-current from a drilling mud discharge. Distribution of mud-associated metals in sediments is extremely uneven, but generally there is a definite gradient of decreasing concentration with distance from the discharge. The greatest enrichment in sediment metal may be directly under the mud discharge or a short distance down-current, depending on current speed and water depth. Major enrichment of sediment metal concentration usually occurs within a distance of about 100 meters or less from the discharge point. Background concentrations are usually reached within 1,000 meters down-current from the discharge. Shunting of drilling muds to near the bottom seems to have only a minor effect on metal concentration in nearby sediments. Concentrations of metals are higher in sediments near the outfall and the gradient of decreasing concentration with distance from the platform is steeper than when muds are discharged at or near the bottom.

TOXICITY OF DRILLING FLUID COMPONENTS

A common practice in evaluating the toxicity of a complex mixture like drilling mud is to determine the toxicity of individual pure components or ingredients of the mixture. The primary purpose of such bioassays is to identify the ingredient or ingredients that cause, or contribute most to the toxicity of the complete mixture. The assumption is made that toxicities of individual ingredients are approximately additive and that physical and/or chemical interactions among ingredients do not take place during formulation or usage of the mixture which might affect the toxicity of the mixture. These assumptions probably are not valid for used treated drilling fluids. Sprague and Logan (1979) showed that the sum of toxicity of individual ingredients of a used drilling fluid was a poor predictor of the acute toxicity of the whole used mud to freshwater fish. A few of the chemical and physical reactions that take place in drilling fluids during usage have been discussed above. Nevertheless, recognizing these limitations, bioassays with drilling mud ingredients are useful for identifying the most toxic ingredients of different types of muds. If particularly toxic or otherwise harmful ingredients are identified they can, in some cases, be replaced by less dangerous substitutes. Muds containing such ingredients can also be prohibited for ocean disposal.

Acute Toxicity

A rather large volume of literature exists on the acute toxicity of drilling mud ingredients to freshwater animals, particularly trout (Logan et al., 1973; Land, 1974; Beckett et al., 1976; Sprague and Logan, 1979). Bioassays in fresh water with freshwater animals cannot be extrapolated to the marine environment, because mechanisms of drilling mud-mediated toxicity appear to be different in marine and freshwater systems. Based on observations of Hrudey (1979) and Sprague and Logan (1979), it appears that the main causes of toxicity of some used drilling muds to freshwater organisms are related to the high pH and high salt concentration (particularly potassium) of the mud. Fresh water has a low ionic concentration (by definition) and is poorly buffered. Freshwater organisms, therefore, generally are very sensitive to changes in pH and ionic concentration of the ambient medium. Seawater, because of its high ionic strength, has a higher buffer capacity. Marine and especially estuarine organisms are more tolerant than freshwater species to small changes in ionic concentration of the medium. Therefore, KCl muds which are quite toxic to freshwater fish, generally show a low order of toxicity to marine species and alkaline muds like most chrome lignosulfonate muds have little effect on seawater pH, except at very high concentrations.

The limited data available on acute toxicity of drilling mud ingredients to marine and estuarine organisms are summarized in Table 13. Of the four major drilling mud ingredients which make up more than 90 percent of most water-based muds (Perricone, 1980), (barite, bentonite, lignite and chrome lignosulfonate), only chrome- and ferrochrome-lignosulfonate show significant toxicity to any but the most sensitive species and life stages of marine organisms. Plant tannins from tree bark and sodium phosphate salts are the other major ingredients which show some toxicity to marine organisms. Other major ingredients are very nearly inert.

Two biocides are included in Table 13. Formaldehyde is moderately toxic and Dowicide G (sodium pentachlorophenate) is extremely toxic. Dowicide B (sodium salt of 2,4,5-trichlorophenol) is also used sometimes as a bactericide in drilling muds (Land, 1974). Its toxicity is likely to be slightly less than that of Dowicide G (Zitko, 1975). Chlorinated phenols are not currently permitted in drilling fluids destined for ocean disposal. Formaldehyde, as paraformaldehyde, is permitted. When used it is maintained in the drilling mud at a concentration of about 700-1,400 ppm (Land, 1974). Thus a 100-fold dilution of the drilling mud will bring its concentration into the sublethal range.

Table 13. Acute toxicity of drilling fluid components to estuarine and marine organisms

Compound	Bioassay Organism	96 Hr LC50(ppm)	Reference
Aquagel® (Wyoming bentonite)	oyster *Crassostrea virginica*	>7,500	Daugherty, 1951
	shrimp *Pandalus hypsinotus*	100,000	Atlantic Richfield, 1978
	copepod *Acartia tonsa*	22,000	Shell Oil Co., 1976
	alga *Skeletonema costatum*	9,600	Shell Oil Co., 1976
Bentonite	oyster *Crassostrea virginica*	110-119 (192 day LC50)*	Cabrera, 1971
Barite (barium sulfate)	several fish and invertebrates	>7,500	Daugherty, 1951
	sailfin molly *M. latipinna*	>100,000	Grantham and Sloan, 1975
	oyster *Crassostrea virginica*	50-60 (216 LC50)*	Cabrera, 1971
	shrimp *Pandalus hypsinotus*	>100,000	Atlantic Richfield, 1978
	copepod *Acartia tonsa*	590	Shell Oil Co., 1976
	alga *Skeletonema costatum*	385-1650	Shell Oil Co., 1976
Calcite (calcium carbonate)	sailfin molly *M. latipinna*	>100,000	Grantham and Sloan, 1975
Siderite (iron carbonate)	sailfin molly *M. latipinna*	>100,000	Grantham and Sloan, 1975
Carbonox® (lignitic material)	several fish and invertebrates	>7,500	Daugherty, 1951
Lignite	sailfin molly *M. latipinna*	>15,000	Hollingsworth and Lockhart, 1975
Chrome-lignosulfonate	sailfin molly *M. latipinna*	12,200	Hollingsworth and Lockhart, 1975
Chrome-treated lignosulfonate	white shrimp *Penaeus setiferus*	465	Chesser and McKenzie, 1975
Ferrochrome-lignosulfonate	Dungeness crab *Cancer magister*	210 (144 Hr LC50)	Carls and Rice, 1980
	Dock shrimp *Pandalus danae*	120 (144 Hr LC50)	Carls and Rice, 1980

Table 13. Continued

Iron-lignosulfonate	white shrimp *Penaeus setiferus*	2,100	Chesser and McKenzie, 1975
Cellulosic calcium carbonate work-over additive	white shrimp *Penaeus setiferus*	1,925	Chesser and McKenzie, 1975
Jelflake® (shredded cellophane)	several fish and invertebrates	>7,500	Dougherty, 1951
Impermex^R (pregelatinized starch)	several fish and invertebrates	500-7500	Daugherty, 1951
	oyster *Crassostrea virginica*	3,000	Daugherty, 1951
Fibertex® (shredded cane fiber)	several fish and invertebrates	>7,500	Daugherty, 1951
Mica	several fish and invertebrates	>7,500	Daugherty, 1951
Low molecular wt. polyacrylate	white shrimp *Penaeus setiferus*	3,500	Chesser and McKenzie, 1975
Quebracho (tannin)	sailfin molly *M. latipinna*	158	Hollingsworth and Lockhart, 1975
Modified hemlock bark extract (tannin)	white shrimp *Penaeus setiferus*	265	Chesser and McKenzie, 1975
Tanio (tannin)	oyster *Crassostrea virginica*	90-170 (108 day LC50)*	Cabrera, 1971
Sodium and pyrophosphate ($Na_2H_2P_2O_7$)	sailfin molly *M. latipinna*	7,100	Grantham and Sloan, 1975
Oilfos® (Na tetraphosphate)	several fish and invertebrates	>7,500	Daugherty, 1951
Quadrafos® (Na polyphosphate)	several fish and invertebrates	500-7500	Daugherty, 1951
Oil well cement	several fish and invertebrates	70-450	Daugherty, 1951
White lime	several fish and invertebrates	70-450	Daugherty, 1951
Formaldehyde	pompano *Trachinotus carolinus*	25-31	Birdsong and Avault, 1971
Dowacide G® (79% Na-pentachlorophenate)	sheepshead minnow *Cyprinodon variegatus* (2 wk. fry)	0.52	Borthwick and Schimmel, 1978
	pinfish *Lagodon rhomboides* (48 hr. prolarvae)	0.066	Borthwick and Schimmel, 1978

*, concentrations are given as ppm turbidity which is usually much lower than ppm material added.

M. = *Mollieniasis*

Formaldehyde is highly volatile and reactive with organic molecules and is readily biodegraded by bacteria when present at low concentration. Thus, it is unlikely to be persistent in the marine environment.

Drilling muds may contain chromium in a variety of chemical forms. Most is tightly bound to lignosulfonate. It is generally believed that virtually all the chromium in a drilling mud that has been used for extended periods will be in the trivalent state, even though it may have been added as inorganic hexavalent chromium salt. Acute toxicity to marine animals of several inorganic trivalent and hexavalent chromium salts is summarized in Table 14. Trivalent chromium salts, primarily because of their extremely low solubilities in seawater, have low toxicities. It is interesting to note, however, that the marine polychaete *Myxicola infundibulum* can detect and respond behaviorally to as little as 1 X 10^{-4} M (5.2 ppm) trivalent chromium (Ward, 1977). Most species of marine animals are much more sensitive to hexavalent chromium salts than to trivalent salts, though there is a great deal of interspecies variation in sensitivity to the former. Sensitivity of blue crabs *Callinectes sapidus* to Cr^{+6} is inversely related to ambient seawater salinity, probably reflecting a change in the chemical form of Cr^{+6} with change in ionic concentration of the medium (Frank and Robertson, 1979). In polychaete worms *Neanthes arenaceodentata*, there is complete inhibition of reproduction at 1.0 ppm and significant reproductive suppression at concentrations as low as 12.5 ppb Cr^{+6} as potassium dichromate (Oshida et al., 1981). By way of comparison, hexavalent chromium appears to be slightly more toxic than trivalent chromium in mammals (Tandon et al., 1978). In fresh water, particularly soft water, trivalent chromium is much more toxic to most species than hexavalent chromium (Land, 1974).

In used chrome lignosulfonate drilling mud, the proportion of total or dissolved chromium which is present in an ionized inorganic form is not known (Liss et al., 1980). As discussed earlier, most of the chromium is

Table 14. Acute toxicity of inorganic trivalent and hexavalent chromium salts to marine animals

Compound	Species	Exposure Time	LC50 (ppm)	Reference
Trivalent Cr				
$CrCl_3$	polychaete *Neanthes arenaceodentata*	293 days	50.4	Oshida et al., 1981
$Cr(NO_3)$	yellow eye mullet *Aldrichetta forsteri*	96 hr	53	Negilski, 1976
Hexavalent Cr				
$K_2Cr_2O_7$	polychaete *Neanthes arenaceodentata*	96 hr	2.22-3.63	Mearns et al., 1976
		168 hr	1.15-1.89	
$K_2Cr_2O_7$	blue crab *Callinectes sapidus*	96 hr (1 o/oo salinity)	34	Frank & Robertson, 1979
		(15 o/oo salinity)	89	
		(35 o/oo salinity)	98	
$K_2Cr_2O_7$	bleak *Alburnus alburnus* (fish)	96 hr	240	Linden et al., 1979
	harpacticoid copepod *Nitocra spinipes*		16	
$K_2Cr\ O_4$	polychaete *Nereis virens*	168 hr	0.7	Eisler & Hennekey, 1977
	crab *Pagurus longicarpus*		2.7	
	clam *Mya arenaria*		8.0	
	starfish *Asterias forbesi*		10.0	
	snail *Nassarius obsoletus*		10.0	
	killifish *Fundulus heteroclitus*		44.0	
$Na_2Cr\ O_4$	yellow-eye mullet *Aldrichetta forsteri*	96 hr	24.0-31.2	Negilski, 1976
	small-mouthed hardyhead *Atherinosoma microstoma*	168 hr	31.6-40.2	
CrO_3	polychaete *Neanthes arenaceodentata*	28 day	0.55-0.70	Reish et al., 1976
	polychaete *Capitella capitata*	96 hr	5.0-8.0	
		28 day	0.28	

probably associated with the lignosulfonate, clay and/or barite fractions of the mud. Thus, the data in Table 14 give no indication of the contribution of chromium to the toxicity of drilling muds.

Another material, used in small amounts in some drilling muds, which could show significant toxicity to marine animals is detergent or surfactant. Detergents are used to aid dispersion in the aqueous phase of the mud of poorly soluble mud components such as aluminum stearate, gilsonite, etc. Polyethoxylated alkyl phenols like Aktaflo-E or Aktaflo-S may be added to drilling muds at concentrations of 1-10 lbs/bbl (API, 1978). Structurally related polyoxyethylene esters and ethers have acute toxicities in the range of 1-40 ppm for Atlantic salmon *Salmo salar* and 2.5-14,000 ppm for the amphipod *Gammarus oceanicus* (Wildish, 1972). Anionic detergents of the linear alkylate sulfonate and alkyl aryl sulfonate types also are used sometimes in drilling muds. They have acute toxicities to freshwater and marine invertebrates and fish of 0.4 to 40 ppm (Abel, 1974). Toxicity increases with decrease in water hardness (or salinity) and decrease in alkyl side chain length.

Chronic and Sublethal Effects

Relatively little research has been performed to date on chronic and sublethal effects of individual drilling mud ingredients to marine animals. Nearly all the research has been performed with barite and various biocides, and strangely enough nothing has been done with chrome lignosulfonate, the only major drilling fluid ingredient exhibiting any acute toxicity to marine animals.

Several experiments were performed on effects of barite or biocides on recruitment from the plankton of benthic invertebrates to sandy sediments in experimental aquaria receiving unfiltered natural seawater (Tagatz and Tobia, 1978; Cantelmo et al., 1979; Tagatz et al., 1980). In barite experiments, aquaria (56 cm by 9 cm by 12 cm high) contained 6 cm clean sand, a 1:10 or 1:3 sand:barite mixture or 5.5 cm sand overlain with a 0.5 cm layer of barite. Unfiltered natural seawater was supplied at a rate of 12 liters/hr.

After ten weeks, abundance, primarily in the upper 2 cm of meiofaunal representatives of the Rotifera, Foraminifera, Hydrozoa, Turbellaria, Ostrocoda, Polychaeta, and Bivalvia was unaffected by the presence of barite (Cantelmo et al., 1979). However, abundances of nematodes, harpacticoid copepods and copepod nauplii were higher in the 1:10 and 1:3 sand:barite mixtures than in pure sand. Nematodes were less abundant in the aquarium containing the 5 mm barite layer over sand than in the control aquarium containing only sand. Highest total meiofaunal abundances were in aquaria containing the sand-barite mixtures.

Macrofauna showed a greater response than meiofauna to barite (Tagatz and Tobia, 1978; Tagatz et al., 1980). A layer of 5 mm barite on the sand substrate significantly reduced recruitment of macroinvertebrates to the aquaria (Table 15). Particularly affected were molluscs (especially *Laevocardium mortoni*) and annelids (especially *Armandia agilis*). Sand-barite mixtures had a much less dramatic effect. Abundances of the dominant polychaetes, *Armandia agilis* and *Prionospio heterobranchia*, were decreased compared to controls by about 50 percent in 1:10 barite:sand. Abundance of annelids in the 1:3 barite:sand mixture was reduced even further. Molluscs and several other taxa were actually more abundant in the 1:10 barite:sand mixture than in the control, so that total numbers of animals and species were slightly, but not significantly higher, in the 1:10 mixture than in the control. A few species occurred only in the sand-barite mixtures.

Table 15. Numbers of animals and species collected from aquaria containing sand alone or sand-barite mixtures and receiving unfiltered natural seawater at a flow rate of 200 ml/minute for 10 weeks (From Tagatz and Tobia, 1978; Tagatz et al., 1980).

Taxon	Number of individuals or species (in brackets)			
	Control	Barite 1:10	Barite 1:3	5mm Barite Cover
Mollusca	474 (21)	611 (17)	413 (17)	210** (12)**
Laevocardium mortoni	268	364	219	114
Anomalocardia auberiana	28	77	84	41
Annelida	368 (14)	233** (18)	54** (11)	33** (10)
Armandia agilis	180	90	10	0
Prionospio heterobranchia	145	85	7	1
Chordata	77 (1)	122 (1)	114 (1)	111 (1)
Molgula manhattensis	77	122	114	111
Other Phyla	47 (8)	65 (10)	39 (8)	49 (10)
Total	966 (44)	1031 (46)	620* (37)	403** (33)**

*, significantly different from control at 5% level; **, significantly different from control at 1% level.

It seems likely that much of the effect of barite on recruitment from the plankton of benthic invertebrates to sandy sediments was due to barium-mediated changes in sediment texture, and not to any chemical toxicity of barite. Barite has a much finer grain size (mean less than 60 μm) than sand. The sand substrate in control aquaria contained no silt-clay fraction, whereas in aquaria containing sand-barite mixtures, the clay-silt fraction was 5.6 to 16.3 percent (Cantelmo et al., 1979). Grain size distribution, mineralogy, texture and organic content of sediments have a profound effect on settlement of planktonic larvae (Thorson, 1957; 1966). A change in sediment characteristics has the effect of rendering the sediment unsuitable for some species, but more suitable for others.

When shrimp *Palaemonetes pugio* were exposed to 500 ppm barite (present primarily as a fine precipitate, since this is far in excess of the solubility of $BaSO_4$ in seawater) for periods up to 106 days, they ingested the barite (Brannon and Rao, 1979; Conklin et al., 1980). Although this did not affect survival of the shrimp, several sublethal responses were observed. Barite ingestion caused damage to the epithelium of the posterior midgut, possibly by abrasion. The shrimp also incorporated grains of barite into statocysts at the time of molting. The shrimp accumulated barium in the exoskeleton and soft tissues. Barium concentration in the carapace of intermolt control shrimp ranged from 67 to 108 mg/kg while barium concentration in the carapace of shrimp exposed for up to 21 days to 500 ppm barite ranged from 202 to 662 mg/kg. Other tissues of barite-exposed shrimp showed similar elevations in tissue barium concentration. Barium is a normal constituent of marine invertebrate tissues and calcified structures (Chow and Snyder, 1980). The chemical form and physiological significance of elevated barium concentrations in barite-exposed animals is unknown.

Thompson and Bright (1977) applied 25 ml of slurries of one part barite in one part water or one part Aquagel (bentonite clay) in two parts water to small colonies of three reef corals, *Diploria strigosa*, *Montastrea cavernosa* and *Montastrea annularis*. This heavily coated the surface of the corals. Despite this extreme treatment, the corals were able to clear their surfaces of the sedimented material rapidly. *D. strigosa* cleared itself faster than the other species. Barite and Aquagel were cleared at about the same rate as natural calcium carbonate sand. Mean clearing rates for the three species of $CaCO_3$, barite and Aquagel were 257, 251 and 293 mm^2/hour, respectively.

These investigations all show that pure barite is not a serious environmental pollutant except when present for extended periods at very high concentration. Barite in used drilling mud interacts with and is partially bound to the clay-lignosulfonate fraction. In this form, its behavior in the marine environment and effect on marine organisms can be expected to be different from that of pure barite.

Tagatz et al. (1980) also studied the effects of three biocides Dowicide G-ST (79% sodium pentachlorophenol, 11% sodium salts of other chlorophenols), Surflo B-33 (37.4% isopropyl alcohol, 17% sodium salt of 2, 2' methylenebis-4,6-dichlorophenol, 8% sodium salts of other chlorophenols) and Aldacide (91% paraformaldehyde), on recruitment of benthic invertebrates to sandy substrata in aquaria. The biocides were metered into the inflowing water at a constant rate. Recruitment to the sand substrate of most species was adversely affected by the two chlorophenol biocides, Dowicide and Surflo, at concentrations in the 10 to 205 μg/ℓ range (Table 16). Molluscs were the only group adversely affected by the 10-18 μg/liter concentrations. The paraformaldehyde biocide, Aldacide, was without effect at concentrations of 14 and 273 μg/liter.

Table 16. Effects of biocides on recruitment from the plankton of benthic macrofaunal invertebrates to sand substrata in aquaria. Biocides were metered into inflowing water to obtain concentrations indicated. (From Tagatz et al., 1980).

Phylum	Biocide Concentration (μg/liter)					
	Dowicide G-ST		Surflo B-33		Aldacide	
	18	183	10	205	14	273
Mollusca	*	*	*	*	NS	NS
Annelida	NS	*	NS	*	NS	NS
Arthropoda	NS	*	-	-	-	-
Chordata	-	-	NS	*	NS	NS
All Phyla	*	*	NS	*	NS	NS

*, number of individuals significantly less than control ($\alpha = 0.05$)

NS, not significantly less than control

-, insufficient numbers collected for statistical analysis.

Chlorinated phenol biocides are obviously quite toxic to benthic invertebrates. However, as stated elsewhere, they are not permitted for use in drilling fluids destined for ocean disposal. Paraformaldehyde at concentrations up to 273 ppb was without significant effect. Aldacide is recommended for use in amounts up to 300 g/bbl (about 1,500 ppm paraformaldehyde). Its rate of loss from discharged used drilling mud by dilution, biodegradation and evaporation would probably be sufficient to maintain its ambient concentration well below toxic levels.

TOXICITY OF USED DRILLING FLUIDS TO MARINE ANIMALS

Bioassay Protocols

A used drilling fluid, especially a treated mud from a deep hole, is an extremely heterogeneous material. It contains water-soluble materials, clay-sized particles of moderate density that sediment slowly in seawater, and high-density particles that sediment rapidly. These fractions tend to separate rapidly when the drilling fluid is added to seawater in a bioassay aquarium or when it is discharged from an offshore drilling rig. This makes it extremely difficult to design a bioassay protocol in which test organisms are exposed uniformly and reproducibly to a drilling mud-seawater mixture of known concentration and/or which will at least roughly simulate the kind of exposure an organism might encounter in the vicinity of the drilling mud discharge from an offshore rig.

The simplest approach has been to add whole drilling mud to seawater on a volume:volume basis to establish several exposure concentrations. Test organisms are exposed to these mixtures which are aerated, mixed or left unmixed during the bioassay (McLeay, 1976; Houghton et al., 1980a; Tornberg et al., 1980).

Another approach is to evaluate toxicity of different drilling fluid fractions on drilling fluid-seawater mixtures which roughly simulate the types of exposure organisms in different marine habitats might encounter. These bioassay protocols are similar to those recommended for evaluation of the environmental impact of dredged material (EPA/COE, 1977). Tables 17 and 18 summarize methods for preparation of drilling fluid bioassay media according to protocols recommended by EPA, Region 2 and according to modified protocols of Neff, et al. (1980, 1981), respectively. Mud:seawater mixtures prepared by the two protocols are quite similar. The LP

Table 17. Methods for preparation of drilling fluid bioassay media according to recommendations of EPA, Region 2 (based on EPA/COE, 1977).

A. Liquid Phase (LP). One part by volume of drilling mud is added to four parts unfiltered seawater. The pH is adjusted, if necessary, to within 0.2 pH unit of seawater pH with acetic acid. The slurry is stirred mechanically and aerated vigorously for 30 minutes. The mixture is allowed to settle for one hour. The supernate is centrifuged and filtered through a 0.45-micron filter. The liquid phase is used immediately in bioassays. The 100% LP contains the water-soluble fraction of 250,000 ppm drilling mud in water.

B. Suspended Particulate Phase (SPP). The suspended particulate phase is prepared in a manner similar to the liquid phase. The suspended particulate phase is the supernate (containing soluble and suspended particulate mud fractions) remaining after the one-hour settling period. It is the uncentrifuged, unfiltered liquid phase. The SPP is used immediately in bioassays. The 100% SPP contains the water-soluble and fine particulate fractions of 250,000 ppm drilling mud in water.

C. Solid Phase (SP). The solid phase is the settled fraction obtained in preparation of the SPP for LP preparation above. After the SPP is decanted the SP is added to aquaria to yield a layer of mud over natural clean sediment. Seawater is usually added and decanted at least once to remove soluble materials. The SP preparation is the insoluble particulate fraction of drilling mud.

Table 18. Methods for preparation of drilling fluid bioassay media according to Neff et al., (1980, 1981).

A. Mud Aqueous Fraction (MAF). One part by volume of drilling mud is added to nine parts artificial seawater (Instant Ocean, Aquarium Systems, Inc.) of the appropriate salinity. The mixture is stirred thoroughly and then allowed to settle for 20 hours. The resulting supernate (100% MAF) is diluted with artificial seawater to the appropriate concentration used immediately. It may be filtered through a 0.45-micron filter to produce a filtered MAF. The 100% MAF contains the water-soluble and fine particulate fractions of 100,000 ppm mud in water.

B. Suspended Particulate Phase (SPP). One part by volume of drilling mud is added to nine parts artificial seawater. The mud-water slurry is air-mixed with filtered compressed air for thirty minutes, with manual stirring every ten minutes. The suspension is then allowed to settle for four hours before the supernate (100% SPP) is siphoned off for immediate use in bioassays. The SPP resembles the MAF except that the SPP contains a higher concentration of particulates and lower concentration of volatiles.

C. Suspended Solids Phase (SSP). Known volumes of drilling mud are added to artificial seawater and the mixture is aerated vigorously during the bioassay to keep particulates in suspension.

D. Layered Solid Phase (LSP). A measured volume of mud is layered over clean natural sediment in an aquarium. Natural seawater is added with minimal resuspension of mud. After 24 hours the water may be decanted and replaced with clean seawater to remove mud solubles. Animals are added after 24-48 hours' settling.

preparation of EPA resembles the MAF and SPP preparations of Neff et al. (1980, 1981). The major difference is the ratio of mud to water used to prepare the stock mixtures.

Flow-through exposure systems also have been used for long-term and sublethal effects studies (Conklin et al., 1980; Krone and Biggs, 1980; Rubinstein et al., 1980). There is danger of fractionation of drilling fluid in such systems, resulting particularly in buildup of heavier mud fractions in exposure tanks. Design of such a system poses several technical problems, some of which have not yet been solved.

In the discussion that follows, primarily for comparison purposes, bioassay results of all but solid phase tests will be expressed in terms of ppm whole mud added initially.

Acute Toxicity

McLeay (1976) studied the toxicity of seven Arctic drilling fluid wastes to seawater-acclimated salmon and four species of Arctic marine intertidal invertebrates (Table 19). Five of the seven drilling mud samples were toxic to seawater-acclimated coho salmon *Oncorhynchus kisutch* at concentrations of less than 5 percent v/v (50,000 ppm). The most toxic drilling mud to salmon had a 96-hr LC50 of 15,000 ppm. With a few exceptions, the four marine invertebrates were more tolerant than salmon to the seven used drilling muds. Acute toxicity, measured as 96-hr. LC50, ranged from 10,000 ppm to greater than 560,000 ppm. No species was consistently more sensitive than the others. The most toxic drilling muds were KCl polymer mud, KCl-XC polymer mud and weighted Shell polymer mud. The weighted gel XC-polymer mud had a consistently very low toxicity for all species tested.

Table 19. Acute toxicity (measured as concentration killing 50 percent of test organisms in 96 hours, (96-hr, LC50) of seven used Arctic drilling fluids to Arctic marine fish and invertebrates. Whole drilling muds were used. Values are in mg/ℓ (ppm) mud added initially (From McLeay, 1976).

Drilling Mud	Coho salmon *Oncorhynchus kisutch*	Marine Worm *Nereis vexillosa*	Softshell Clam *Mya arenaria*	Purple Beach Crab *Hemigrapsus nudus*	Sand Flea *Orchestia traskiana*
Shell Kipnik, KCl polymer	29,000	37,000	42,000	53,000	-
Aquitaine et al. Polar bear, seawater polymer	130,000	220,000	320,000	530,000	230,000
Sun Bux et al Pelly, KCl-XC polymer	23,000	41,000	56,000	78,000	14,000
Shell Niglintgak, weighted Shell polymer	15,000	23,000	10,000	62,000	80,000
Sun Bux et al Pelly, gel chemical-XC	39,000	>560,000	>560,000	>560,000	80,000
Sun Bux et al Pelly, weighted gel XC-polymer	190,000	320,000	>560,000	560,000	420,000
Dome Imp Imnak, gel XC-polymer	30,000	200,000	>560,000	>560,000	>560,000

Toxicity of four used offshore drilling muds to marine animals was studied in some detail by Gerber et al. (1980) and Neff et al. (1980, 1981). These muds were obtained from offshore drilling sites in the Gulf of Mexico. Composition of the drilling muds is summarized in Table 20.

The used seawater chrome lignosulfonate mud (CLS) was extensively studied by Neff et al. (1981). Table 21 summarizes results of bioassays with ten species of marine invertebrates and the mud aqueous fraction of CLS mud. Acute toxicity of the static MAF, measured as 96-hr. LC50, ranged from 32% to greater than 100% of the MAF. Since the MAF represents the soluble and fine particulate fractions of one part mud in nine parts seawater, these concentrations correspond to 32,000 to greater than 100,000 ppm mud added. When the MAF was filtered through a 0.45 μm filter (FMAF), it lost little of its toxicity, indicating that a majority of the toxicity of the MAF resided in the soluble portion. If the MAF was changed daily during the 96-hr bioassay, its toxicity was much higher than that of the static MAF, indicating that some of the toxic components of the MAF were lost from the bioassay containers under static conditions, probably by volatilization. Analysis of the bioassay mixtures revealed that, whereas the concentration of chromium in the MAF did not change significantly with time, the concentration of hexane-extractable, UV-absorbing "aromatic hydrocarbons" decreased rapidly in the static MAF. This apparently volatile material, which may include petroleum aromatics and UV-absorbing by-products and degradation products of lignosulfonate and lignite, appears to contribute significantly to the acute toxicity of the MAF. Gerber, et al. (1980) reported high concentrations of petroleum hydrocarbons in this mud.

Table 20. Composition of used drilling muds evaluated by Gerber et al., (1980) and Neff et al. (1980, 1981)

Seawater Chrome Lignosulfonate Mud (CLS):

Major components: seawater, bentonite clay, chrome lignosulfonate, lignite, caustic soda ($NaOH$), and barite ($BaSO_4$).

Mid-Weight Lignosulfonate Mud (MWL):

Major components: freshwater, bentonite clay, chrome-lignosulfonate, lignite caustic soda, lime ($Ca(OH)_2$), and barite.

Minor components: defoamer, oxygen scavenger, walnut lost circulation material, and gilsonite (a natural bituminous material).

High Weight Lignosulfoante Mud (HWL):

Major components: freshwater, bentonite clay, chrome-lignosulfonate, lignite caustic soda, soda ash (Na_2CO_3), sodium bicarbonate, polyanionic cellulose derivative, and barite.

Minor components: defoamer, lubricant, and mica lost circulation material.

Spud Mud (Spud):

Major components: freshwater, bentonite clay and caustic soda.

Minor components: barite.

Table 21. Acute toxicity of the mud aqueous fraction (MAF) of a used chrome lignosulfonate drilling mud to several species and life stages of marine animals. All 96-hour LC50 data are expressed as ppm mud added (Data from Neff et al., 1981).

Species	Life Stage	Type of Exposure[1]	96-Hr. LC50
Marine worm			
Neanthes arenaceodentata	Juveniles	Static MAF	96,000
		Static FMAF	>100,000
	Adults	Static MAF	51,000
		MAF changed daily	10,000
Marine worm			
Ophryotrocha labronica	Adults	Static MAF	>100,000
		Static FMAF	>100,000
Marine worm	Adults	Static MAF	32,000
Dinophilus sp.		Static FMAF	45,000
Opossum shrimp			
Mysidopsis almyra	1 day old	MAF changed daily	27,000
		Static MAF	40,000
	3 day old	Static MAF	79,000
	7 day old	Static MAF	73,000
	14 day old	Static MAF	96,000
Grass shrimp			
Palaemonetes pugio	4 day old	Static MAF	34,000
	Post-larvae	Static MAF	67,000
	Adults	Static MAF	90,000
Pink shrimp			
Penaeus duorarum	Post-larvae	Static MAF	86,000
Coquina clam			
Donax variabilis	Juveniles	Static MAF	>100,000
	Adults	Static MAF	86,000
Hard-shell clam			
Mercenaria campechiensis	Adults	Static MAF	>100,000
Marsh clam			
Rangia cuneata	Adults	Static MAF	>100,000

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1. Static MAF, the MAF was not changed during the 96-hour bioassay; Static FMAF, the MAF was filtered through a 0.45μm filter and aerated before use in the bioassay; MAF changed daily, MAF was replaced every 24 hours with freshly prepared exposure medium.

Tolerance of mysid shrimp and grass shrimp to the MAF increased with age of the animals. However, adults of the marine worm *Neanthes arenaceodentata* were more sensitive than juveniles of the same species.

The suspended solids phase (SSP) preparation of used CLS mud was toxic to young pink and brown shrimp *Penaeus duorarum* and *P. aztecus* at a concentration of 10 ml/liter (equivalent to 10,000 ppm) (Table 22). The suspended solids phase preparation was somewhat more toxic to young penaeid shrimp than the mud aqueous fraction, indicating that the settleable particles, present in the SSP and not in the MAF, contribute to the toxicity of the drilling mud to sensitive species, perhaps by clogging the gills and interfering with respiration. The three other species examined, an oceanic crab and two bivalve molluscs, were unaffected by exposure to 20 ml/l (20,000 ppm) SSP preparation.

Five species of marine invertebrates varied substantially in their sensitivity to the layered solids phase (LSP) preparation of the used chrome lignosulfonate drilling mud (Table 23). Adult marine worms *Neanthes arenaceodentata* and adult coquina clams *Donax variabilis* seemed to be quite sensitive to this mud preparation, whereas the other species and life stages tested were more tolerant. The concentrations used in this bioassay produced a layer of drilling mud 5 to 20 mm thick on the sand substrate of the exposure tank.

Mud aqueous fractions of the four used drilling muds varied in their toxicity to several species of marine animals from the Gulf of Mexico (Neff, 1980; Neff et al., 1980). The mud aqueous fraction of the used spud mud was not acutely toxic to the three species tested (Table 24). The 100% MAF failed to produce any mortality in 96 hours. In most cases, the MAF of the mid-weight lignosulfonate drilling mud was more toxic than the MAF of the seawater chrome lignosulfonate mud and the high weight lignosulfonate mud. The 96-hr LC50 of the MAF of the three used chrome lignosulfonate muds ranged from 7.5% MAF

Table 22. Results of bioassays with five species of marine invertebrates exposed to the suspended solids phase (SSP) of a used chrome lignosulfonate drilling mud. Exposure concentrations are in mg mud/liter of seawater (ppm). n = number of animals per treatment (From Neff et al., 1981).

	Species				
	Penaeus duorarum	*Penaeus aztecus*	*Portunus spinicarpus*	*Mercenaria campechiensis*	*Rangia cuneata*
Life stage	Postlarvae	Juveniles	Adults	Adults	Adults
Exposure concentration (mg/ℓ)	10,000	10,000	20,000	20,000	20,000
Salinity (o/oo)	28	28	35	20	20
n	25	10	6	5	25
Exposure period (hrs.)	168	168	168	96	96
Percent survival	71	40	100	100	100

Table 23. Results of bioassays with five species of marine invertebrates exposed to the layered solid phase (LSP) of a used chrome lignosulfonate drilling mud. Exposure concentrations are in ml mud/liter seawater. n = number of animals per treatment (From Neff et al., 1981).

	SPECIES						
	Marine Worm *Neanthes arenaceodentata*		Marine Worm *Ophryotrocha labronica*	Opossum Shrimp *Mysidopsis almyra*	Coquina Clam *Donax variabilis texasiana*		Scallop *Aequipecten amplicostatus*
Life stage	Juveniles	Adults	Adults	1 day	Juveniles (<1 cm)	Adults (>2 cm)	Adults
Exposure concentration (ml/l)	40	40	50	25	100	100	20
Salinity (o/oo)	32	32	34	20	35	35	20
n	40	25	20	100	25	25	10
Exposure period (hrs)	96	96	96	168	96	96	96
Percent survival	77.5	25	95	55	32	0	40

Table 24. Acute toxicity of the mud aqueous fraction (MAF) of four used drilling muds to several species of marine animals. All 96-hour LC50 values are expressed as ppm mud added. Exposure media were changed daily during bioassays (From Neff, 1980).

Species	Life Stage	Mud Types[1]			
		CLS	MWL	HWL	Spud
Hermit Crab *Clibanarius vitattus*	Adults	28,700	34,500	65,600	-[2]
Brown shrimp *Penaeus aztecus*	Juveniles	41,500	16,000	-	-
Blue crab *Callinectes sapidus*	Adults	-	-	>100,000	-
Grass shrimp *Palaemonetes pugio*	1st Zoeae	7,500	35,000	<18,000	>100,000
	Adults	92,400	91,000	>100,000	>100,000
Opossum shrimp *Mysidopsis almyra*	1 day old	27,000	12,800	<16,000	>100,000
	7 day old	-	13,000	32,500	>100,000
Marine worm *Ophryotrocha labronica*	Adults	100,000	60,000	>100,000	>100,000
Killifish *Fundulus heteroclitus*	43 day fry	-	-	80,000	-
Gulf killifish *Fundulus similis*	Adults	-	-	>100,000	-

1, CLS, seawater chrome lignosulfonate mud; MWL, midweight lignosulfonate mud; HWL, high weight lignosulfonate mud; Spud, spud mud.

2, no bioassay performed.

(12,800 ppm mud added) for first day postlarvae of opossum shrimp to greater than 100% MAF (>100,000 ppm) for adult grass shrimp *Palaemonetes pugio*, marine worms *Ophryotrocha labronica*, blue crabs *Callinectes sapidus*, and Gulf killifish *Fundulus similis*.

Mud aqueous fractions of these muds plus a low density lignosulfonate mud from the Baltimore Canyon were somewhat less toxic to marine animals from the coast of Maine (Gerber et al., 1980, 1981) than to species from the Gulf of Mexico. Most species were unaffected by the 100% MAF of any of the five drilling muds (Table 25 and 26). Among the crustaceans, stage 1 and III larvae of shrimp *Pandalus borealis* and stage V larvae of lobsters *Homarus americanus* were sensitive to the MAF preparations to which they were exposed. The copepod *Eurytemora herdmani* was moderately sensitive to the MAF of midweight and low weight drilling muds but not to the MAF of spud mud.

The toxicity of the suspended particulate phase (SPP) preparation of the drilling muds was also evaluated (Table 27; Neff et al., 1980). The acute toxicity of the SPP of the lignosulfonate muds ranged from 11.7-74% SPP (11,700-74,000 ppm mud added). The spud mud SPP was not acutely toxic. Adult coquina clams *Donax variabilis* were more sensitive than juvenile Pacific oysters *Crassostrea gigas* to the lignosulfonate muds. Different stage larvae of *Palaemonetes pugio* were equally sensitive to the SPP preparation of the HWL mud. Much of the toxicity of these muds appears to reside in the water-soluble fraction of the mud, as indicated by the observation that 96-hr. LC50s for the MAF and SPP of high weight lignosulfonate mud were similar for the grass shrimp *Palaemonetes pugio*.

Male amphipods *Gammarus locusta*, lobsters *Homarus americanus*, and ocean scallops *Placopecten magellanicus* were sensitive to a substrate composed of a mixture of drilling mud and natural marine sediment (Tables 26 & 28; Gerber

Table 25. Acute toxicity, expressed as 96-hour LC50, of the mud aqueous fraction (MAF) of five used offshore drilling muds to cold-water species of marine animals from Maine. All values are in ppm mud added (Data from Gerber et al., 1980).

	Mud Type[1]				
Species	HWL	MWL	LWL	CSL	Spud
Crustaceans:					
Crangon septemspinosa	>100,000	>100,000	98,000	>100,000	>100,000
Gammarus locusta	>100,000	>100,000	-	-	>100,000
Pandalus borealis (Stage 1)	65,000	17,000	-	-	-
Carcinus maenas	>100,000	>100,000	>100,000	-	-
Homarus americanus (Stage V)	-	-	5,000	-	-
Homarus americanus (Adult)	-	>100,000	>100,000	-	-
Bivalve Molluscs:					
Mytilus edulis	>100,000	>100,000	-	>100,000	>100,000
Macoma balthica	>100,000	-	>100,000	-	-
Gastropod Molluscs:					
Littorina littorea	>100,000	>100,000	>100,000	-	-
Thais lapillis	-	-	>100,000	-	-
Polychaete Worms:					
Nereis virens	>100,000	>100,000	>100,000	>100,000	>100,000
Echinoderms					
Strongylocentrotus droebachiensis	-	>100,000	>100,000	-	-
Fish:					
Fundulus heteroclitus	>100,000	>100,000	-	>100,000	>100,000

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1. HWL, high weight lignosulfonate mud; MWL, midweight lignosulfonate mud; LWL, low weight lignosulfonate mud; CLS, seawater chrome lignosulfonate mud; Spud, spud mud.

Table 26. Results of the bioassays on marine organisms exposed to various fractions of used medium and light weight lignosulfonate drilling mud and a spud mud. Unless specified all animals are adults. MAF = mud aqueous fraction, WM = whole mud substrate, WMW = washed whole mud substrate, SSP = suspended solid phase, N = number of animals per treatment. LC50 values are given as the ppm of MAF, WM, WMW or SSP. (From Gerber et al., 1981).

			LC 50 values							
			MAF		WM		WMW		SSP	
Species	n	Temp.	96 hrs.	168 hrs.	96 hrs.	168 hrs.	96 hrs.	168 hrs.	96 hrs.	163 hrs.
Medium Density Drilling Mud										
Homarus americanus	16	10-12°C	>100000	84000	290000	180000	850000	780000		
Panadalus borealis (Stage III)	24	4°C	13000						40000	
Cancer borealis	25	5°C	>100000		960000		380000			
Eurytemora herdmani	40	4°C	82000	60000					620000	380000
Eurytemora herdmani	38	16-17°C	59000	50000					320000	200000
Placopecten magellanicus	32	10°C	>100000	92000	5000		20000		60000	50000
Placopecten magellanicus	20	4.5°C	>100000	>100000	7000	3000	30000	10000		
Light Density Drilling Mud										
Eurytemora herdmani	21	4°C	83000	77000					800000	650000
Eurytemora herdmani	24	16-17°C	67000	56000					580000	580000
Spud Mud										
Eurytemora herdmani	21	4°C	>100000	>100000					980000	940000

Table 27. Toxicity of the suspended particulate phase (SPP) preparation of four used offshore drilling muds to adult coquina clams *Donax variabilis texasiana*, two size classes of spat of the Pacific oyster *Crassostrea gigas*, and 1-, 5- and 10-day-old zoeae of the grass shrimp *Palaemonetes pugio*. Ninety-six-hour LC50 values are in ppm SPP preparation added (Data from Neff, et al., 1980).

	Mud Type[1]			
Species	CLS	MWL	HWL	Spud
Donax variabilis (Adults)	53,700	29,000	56,000	im[2]
Crassostrea gigas (3-10 mm)	-	53,000	74,000	im
Crassostrea gigas (10-25 mm)	-	50,000	73,000	im
Palaemonetes pugio (1 day old)	-	-	11,800	-
(5 day old)	-	-	13,200	-
(10 day old)	-	-	11,700	-

1. CLS, chrome lignosulfonate mud; MWL, mid-weight lignosulfonate mud; HWL, highweight lignosulfonate mud; spud mud.

2. im, insufficient mortality to compute LC50 value.

Table 28. Acute toxicity, expressed as 96-hour LC50, of the layered solids phase preparation of four used offshore drilling muds to cold-water species of marine animals from Maine. These were flow-through bioassays with flow rates of 10-20 liters per hour. Values are expressed as percent of whole mud in natural marine substrate (From Gerber et al., 1980).

	Mud Type[1]			
Species	HWL	MWL	LWL	Spud
Crustaceans				
Crangon septemspinosa	92	82	71	-
Gammarus locusta (males)	28	74	-	>100
Gammarus locusta (females)	88	90	-	>100
Carcinus maenas	>100	68	89	-
Homarus americanus (adult)	-	29	19-25	-
Bivalve Molluscs:				
Macoma balthica	>100	-	>100	-
Placopecten magellanicus	-	<3.2[2]	49	-
Gastropod Molluscs:				
Littorina littorea	>100	>100	-	-
Thais lapillis	-	-	83	-
Polychaete Worms:				
Nereis virens	100	>100	>100	-
Echinoderms:				
Strongylocentrotus droebachiensis	-	>100	55	-

1. HWL, high weight lignosulfonate mud; MWL, midweight lignosulfonate mud; LWL, low weight lignosulfonate mud; spud, spud mud.

2. This value is in ml of mud/liter of seawater and represents a 1-mm thick layer spread over natural mud in the aquarium.

et al., 1980, 1981). Even in these cases, a 20-30% drilling fluid-sediment mixture or a 1-mm layer of pure whole mud was required to produce 50% mortality. The most surprising observation was that several species could tolerate a 100% drilling mud substrate for 96 hours.

Ocean scallops *Placopecten magellanicus* were quite tolerant to the MAF but very sensitive to whole mud or washed whole mud in the substrate. These results suggest that scallops are very sensitive to fine suspended particulates. The 168-hr. LC50 for whole drilling mud in the substrate was 0.3 percent (equivalent to 3,000 ppm mud in sediment). Scallops and larval shrimp also were sensitive to suspended solids phase preparations, tending to support the hypothesis of sensitivity to fine particulates.

The toxicity of the five typical used offshore drilling fluids has been evaluated in 27 species representing five major animal phyla. The results are consistent in showing that typical used offshore drilling muds have a low order of acute toxicity to a wide variety of species and life stages of marine animals. Even for the most sensitive species and life stages, 96-hr. LC50 values were rarely lower than 10,000 ppm mud added for the most toxic muds.

To comply with bioassay requirements stipulated in NPDES permits issued for exploratory drilling in lease areas 40 and 49 on the Middle Atlantic outer continental shelf, a Joint Bioassay Monitoring Program was established by the Offshore Operators Committee. Eight used drilling muds of different types, all typical of those to be used in OCS exploratory drilling activities, were evaluated using mysid shrimp (*Mysidopsis bahia*) (liquid and particulate phase bioassays) and hard shell clams *Mercenaria mercenaria* (solid phase bioassays).

Composition of the muds is summarized in Appendix I, Tables1a-8a). Results of bioassays by ERCO, Inc. (1980) are summarized in Table 29. Results of bioassays on mud No. 1 were not available at this writing. Only two liquid-phase preparations were acutely toxic to the shrimp (the seawater lignosulfonate mud, #2 and lime mud, #3). Mysid shrimp are considered to be very sensitive to high suspended particulate concentrations. This is confirmed by the observation that four of the suspended particulate phase preparations were acutely toxic to the shrimp. The most toxic (#2) had a 96-hr. LC50 of 10,640 ppm mud added. The other three mud preparations failed to produce 50 percent mortality in 96 hours in this very sensitive species. None of the solid phase preparations were toxic to the clams. The only preparation producing mortality significantly higher than that of controls was the solid phase of mud #2. This may reflect more the unsuitability of *Mercenaria mercenaria* as a bioassay organism than the low toxicity of solid phase preparations of drilling mud. These clams can remain isolated, by closure of their shells, from an ambient medium they deem noxious for several days.

Tornberg et al. (1980) examined the acute toxicity of four types of used offshore drilling fluids from rigs in the Prudhoe Bay, Alaska area to marine animals from the Beaufort Sea. Composition of the drilling fluids is summarized in Appendix I, Table 9a. The 96-hr. LC50 values for polychaete worms (*Melaenis loveni*), isopod crustaceans (*Saduria entomon*) and snails (*Natica clausa*, *Neptunea* sp., and *Buccineum* sp.) ranged from about 40 to more than 70 percent (v/v) whole mud (400,000-700,000 ppm). LC50 values for mysid shrimp (*Mysis* sp.) and amphipod crustaceans (*Onismus* sp. and *Boeckosimus* sp.) were 6-22 percent and 22-38 percent v/v drilling mud (60,000 - 220,000 ppm and 220,000-380,000 ppm), respectively. Four species of marine fish were also examined. The most sensitive was the fourhorn sculpin (*Myoxocephalus quadricornis*) with 96-hr. LC50 values ranging from 4-35 percent used mud (40,000-350,000 ppm). There was a tendency for drilling mud toxicity to increase with drill hole depth. The

Table 29. Results of bioassays on six used drilling fluids typical of those used for exploratory drilling in the mid-Atlantic OCS lease areas nos. 40 and 49. Mysid shrimp *Mysidopsis bahia* were used for the liquid and suspended particulate phase bioassays. The hard shell clam *Mercenaria mercenaria* was used for solid phase bioassays. Values for 96-hour LC50 in mysid bioassays are in ppm mud added and in clam bioassays, results are given in percent survival at 96 hours (From ERCO, Inc., 1980).

Drilling Fluid Type	96-Hr LC50 (PPM)		
	Liquid Phase	Suspended Particulate Phase	Solid Phase % Survival
#2, Seawater lignosulfonate mud	56,700	10,640	83*
#3, Lime mud	78,600	13,200	100
#4, Nondispersed mud	>200,000(91.7)[1]	>200,000(86.7)*	100
#5, Seawater spud mud	>200,000(98.3)	>200,000(96.7)	100
#6, Saltwater/freshwater gel mud	>200,000(88.4)	44,800	100
#7, Lightly treated lignosulfonate freshwater/seawater mud	>200,000(51.7)*	>200,000(55)*	97
#8, Lignosulfonate freshwater mud	>200,000(95)	101,200	99

*, Significantly lower survival at highest concentration tested than among controls.

1, Percent survival at 96 hours in 100% phase (=200,000 ppm mud).

most toxic mud tested was a CMC/Gel/Resin mud from 2,786 meters drilling depth (Table 30). The authors concluded that sedentary species were less sensitive than pelagic species to the used drilling fluids.

Similar results were obtained by Houghton et al. (1980a) with drilling fluids from the Lower Cook Inlet, Alaska C.O.S.T. well. A high-density lignosulfonate mud system (200,000-250,000 ppm barite, 3,200-5,700 ppm ferrochrome lignosulfonate) was examined. Two species of fish (pink salmon fry *Oncorhynchus gorbuscha* and staghorn sculpin *Leptocottus armatus*) and five species of marine invertebrates (coonstripe shrimp *Pandalus hypsinotus*, mysid shrimp *Neomysis integer*, amphipods *Anisogammarus confervicolus*, isopods *Gnorimosphaeroma oregonensis*, and mussels *Modiolus modiolus*) were tested (Table 31). The most sensitive species were the pink salmon (96-hr. LC50, 0.3-2.9 percent whole mud - 3,000-29,000 ppm) and mysid shrimp (96-hr. LC50, 1-15 percent whole mud - 10,000-150,000 ppm). The effect of stirring and/or aeration on the toxicity of the drilling muds was inconsistent.

Carls and Rice (1980) studied the toxicity of six new and used offshore drilling muds from Alaska to six species of Stage I larvae of crabs and shrimp. Cessation of swimming was used as an index of sublethal response expressed as median effective concentration (EC50). Mortality and behavioral responses were delayed. Behavioral responses were not observed for 4 to 24 hours after the beginning of exposure, whereas measureable mortality did not begin until 48-72 hours of exposure. The most toxic mud was a used mud from the 3,382 meter depth in Cook Inlet, Alaska. It was a ferrochrome lignosulfonate mud. The most sensitive species was the dock shrimp *Pandalus danae* (Table 32). Acute toxicity, measured as 144-hr. LC50, ranged from 0.05 to 0.94% whole mud suspension (500 to 9,400 ppm). Toxicity of water-soluble fractions (WSF) of Cook Inlet mud (the aqueous fraction of a 1:1 seawater:drilling mud

Table 30. Relationship between drilling mud type, well depth and toxicity of whole drilling muds to Arctic marine animals (From Tornberg et al., 1980).

Drilling Fluid Type	Well Depth	Species	96-Hr. LC50 (ppm)
CMC/Gel	1803	saffron cod *Eleginus navaga*	≈235,000
	1807	shrimp *Mysis* sp.	215,000
	2780	Arctic cisco *Coregonus nasus*	>200,000
	2786	fourhorn sculpin *Myoxocephalus quadricornis*	>120,000
XC-Polymer	2778	Arctic cisco *C. nasus*	≈350,000
	3057	Arctic cod *Boreogadus saida*	>250,000
	3064	shrimp *Mysis* sp.	161,000
	3064	fourhorn sculpin *M. quadricornis*	215,000
	3065	shrimp *Mysis* sp.	≈135,000
	3319	fourhorn sculpin *M. quadricornis*	>200,000
	3319	Arctic cisco *C. nasus*	64,000
	3329	Arctic cisco *C. nasus*	100,000
	3646	shrimp *Mysis* sp.	≈ 75,000
	3646	fourhorn sculpin *M. quadricornis*	≈ 75,000
CMC/Gel/ Resinex	2786	fourhorn sculpin *M. quadricornis*	≈ 50,000
	2786	shrimp *Mysis* sp.	< 60,000
	3466	shrimp *Mysis* sp.	73,000
	3466	fourhorn sculpin *M. quadricornis*	≈ 60,000
XC-Polymer/ Unical	3785	amphipods *Onisimus* sp. & *Boeckosimus*	381,000
	3938	amphipods	280,000
	4029	amphipods	278,000
	4175	amphipods	241,000
	4175	amphipods	221,000

Table 31. Acute toxicity of a used high density ferrochrome lignosulfonate drilling mud to marine animals from Cook Inlet, Alaska. LC50 values for whole mud bioassays are given in ppm mud added (From Houghton et al., 1980a).

Species	No. of Bioassays	Bioassay Duration (Hrs.)	LC50
Shrimp *Pandalus hypsinotus*	1	48	between 50,000 & 100,000
	6	96	32,000-150,000
Amphipods *Annisogammarus confervicolus*	2	48	between 10,000 & 50,000
	2	96	>70,000 & >200,000
Mysids *Neomysis integer*	2	48	>74,000-≈125,000
	2	96	between 10,000 & 125,000
Isopod *Gnorimosphaeroma oregonensis*	1	96	>70,000
Mussel *Modiolus modiolus*	1	326	>30,000
Sculpin *Leptocottus armatus*	1	48	between 100,000 & 200,000
Pink salmon fry *Oncorhynchus gorbuscha*	3	96	3,000-29,000

Table 32. Toxicity to stage I larvae (less than 3 days old) of shrimp and crabs of a used ferrochrome-lignosulfonate drilling mud from Cook Inlet, Alaska. Toxicity was measured by mortality (144 hr. LC50) and cessation of swimming (144 hr. EC50). Bioassays were performed with whole mud-in-seawater suspensions (SM) and water-soluble fractions (WSF) of drilling mud. LC50, EC50 concentrations and their 95% confidence intervals are given in ppm mud added by volume (From Carls and Rice, 1980).

Species	LC50		EC50	
	SM	WSF	SM	WSF
King crab	4,800	16,700	2,800	12,900
(*Paralithodes camschatica*)	3,500-6,100	5,600-27,800	0-5,700	8,100-17,700
Dungeness crab	2,000	7,050	NC	NC
(*Cancer magister*)	1,600-2,300	0-19,250		
Tanner crab	9,400	8,250	NC	2,800
(*Chionoecetes bairdi*)	0-62,500	2,000-14,500		1,750-3,850
Kelp shrimp	4,400	2,350	<5,000	NC
(*Eualus suckleyi*)	3,600-5,300	1,200-3,450		
Coonstripe shrimp	*	4,500	≤ 2,000	3,250
(*Pandalus hypsinotus*)		2,700-6,350		2,300-4,150
Dock shrimp	500	1,500	500	1,050
(*Pandalus danae*)	500-500	0-7,650	200-800	800-1,450

*, not tested; NC, not calculable.

mixture) ranged from 0.30 to 3.34% WSF (equivalent to 1,500 to 16,700 ppm mud added). Behavioral responses were observed at slightly lower concentrations. The shrimp larvae were more sensitive than the crab larvae to the water-soluble extracts of the drilling mud. However, dungeness crab larvae were more sensitive than kelp shrimp larvae to the whole drilling mud-seawater suspension. This may indicate that dungeness crab larvae are sensitive to high-suspended particulate concentrations.

The toxicity of the drilling mud WSF decreased slightly with time indicating, as Neff et al. (1980, 1981) have suggested that volatile ingredients contribute significantly to the toxicity of aqueous extracts of drilling muds.

The other five muds, which included used and unused Prudhoe Bay mud, used and unused Homer spud mud, and used Homer mud, from 442 meters, were, with the exception of the new Prudhoe Bay mud substantially less toxic to the larvae than the used Cook Inlet mud (Table 33). The authors estimated that 81±16% of the toxicity of the drilling fluids was due to the particulate fraction of the mud. The remaining 19% of the toxicity was attributed to the soluble components of the mud. They also estimated that ferrochrome lignosulfonate contributed most to the toxicity of the muds. Based on delayed response of at least 4 hours of larvae to the drilling muds and the concentrations required to cause mortality, the authors concluded that discharged drilling fluids would have little or no deleterious impact on planktonic larvae of shrimp and crabs.

Summary of Acute Bioassay Results

In the acute bioassays described above, toxicity of more than twenty used offshore-type drilling fluids were evaluated with 58 species of marine animals from the Atlantic and Pacific Oceans, the Gulf of Mexico and the Beaufort Sea. Five major marine animal phyla were represented among the bioassay organisms, including Chordata (8 species of fish), Arthropoda (31 species of

Table 33. Comparative acute toxicity of six Alaskan offshore drilling muds to stage I larvae of king crab *Paralithodes camschatica* and coonstripe shrimp *Pandalus hypsinotus*. 144-hr. LC50 values for the drilling mud water-soluble fractions are expressed as ppm mud added (Data from Carls and Rice, 1980).

Drilling Mud	Depth (m)	Specific Gravity (g/ml)	WSF 144-Hr. LC50 (ppm) king crab	coonstripe shrimp
Used Prudhoe Bay	2,926	1.122	-	76,550
New Prudhoe Bay	-	1.183	11,650	16,150
Used Cook Inlet	3,382	1.655	16,700	4,500
Used Homer spud	-	1.168	47,250	-
New Homer	-	1.174	35,850	<25,000
Used Homer	442	1.067	150,400	188,100

crustaceans), Mollusca (12 species of molluscs), Annelida (6 species of polychaetes), and Echinodermata (one species of sea urchin). Larvae and other early life stages (considered to be more sensitive than adults to pollutant stress) were included.

Although bioassay methods and conditions varied considerably, the results were surprisingly consistent. All but a few of the 96-hr. LC50 values were above 10,000 ppm drilling mud added. The lowest LC50 value was 500 ppm whole mud for larvae of dock shrimp *Pandalus danae* exposed to a high density lignosulfonate mud from Cook Inlet, Alaska (Carls and Rice, 1980). Other relatively sensitive species included pink salmon fry *Oncorhynchus gorbuscha*, lobster *Homarus americanus* larvae, ocean scallops *Placopecten magellanicus*, and mysid shrimp (*Mysidopsis*, *Neomysis*, and *Mysis*). The authors, in most cases, attributed the sensitivity of these species to their intolerance of high suspended particulate concentrations.

McFarland and Peddicord (1980) examined the acute toxicity to several species of Pacific Coast marine animals of suspended clay (Kaolin, median particle size 4.5 μm). They found that organisms restricted to muddy bottoms were very insensitive to high suspended clay concentrations. On the other hand some species of open-water fish, fouling organisms, and sandy bottom epifauna were relatively sensitive, though some species from these groups were quite tolerant. The most sensitive species tested, the shiner perch *Cymatogaster aggregata*, had a 100-hr. LC50 of 6,000 ppm suspended clay. Eight species experienced less than 10 percent mortality following exposure to suspended clay for 5 to 12 days. These results are remarkably similar to those for many of the drilling muds tested, suggesting that for some intolerant species, damage is caused by mechanical abrasion or physical clogging of delicate respiratory surfaces by fine particulates.

Since mud aqueous fractions and liquid phase preparations were also slightly toxic to some species, it is apparent that used drilling muds possess some chemical toxicity and this is low (96-hr. LC50 greater than 10,000 ppm mud added in most cases). The chemical and mechanical toxicity of the muds appear, at most, to be additive or somewhat less than additive. There is no evidence of synergistic interaction.

Chronic and Sublethal Effects

Rubinstein et al. (1980) exposed mysid shrimp *Mysidopsis bahia*, oysters *Crassostrea virginica* and lugworms *Arenicola cristata* to used drilling fluids from Mobile Bay, Alabama (see Table 4) at nominal concentrations of 10, 30, and 100 ppm for up to 100 days in a flow-through bioassay system. There was 17 percent mortality among mysids exposed to nominal concentrations of 30 and 100 ppm used mud for ten days. Lugworms had high mortalities after 100 days at all drilling mud concentrations. There was 33 percent mortality at 10 ppm mud and 75 percent mortality in 100 ppm mud. However, the design of the flow-through exposure system was such that a layer of drilling mud accumulated on the surface of the sand in the aquaria. At 100 days, this layer of drilling mud ranged from 4.5 mm at a nominal 10 ppm exposure concentration to 10.7 mm at a nominal 100 ppm exposure concentration. Thus a benthic infaunal organism like the lugworm which feeds on surface sediments was actually exposed to very much higher concentrations of mud particulates than the nominal mud concentrations would imply.

This same argument could be used in reference to several of the static bioassays with whole mud described above where mud particulates tended to settle on bioassay organisms on the bottom of exposure tanks. The effect of this is that actual exposure concentrations were higher than nominal ones, making actual LC50 values higher than estimated. As indicated by the authors, the apparent sensitivity of lugworms to drilling fluid could be due to intolerance to textural changes in substrate caused by accumulation of drilling mud on and in the sand, or to chemical toxicity of some drilling fluid constituents.

Exposure to the drilling mud also significantly inhibited rate of regeneration of the shell in young oysters from a mean of 3.79 mm per week among controls to 2.99 mm per week at a nominal 100 ppm drilling mud. As indicated above, actual exposure concentrations were higher due to accumulation of mud particulates.

Conklin et al. (1980) evaluated the acute and chronic toxicity and sublethal effects of drilling muds collected at eighteen depth intervals from an exploratory well in Mobile Bay, Alabama. These were the same drilling muds as those used by Rubinstein et al. (1980). None of the drilling muds was toxic to intermolt grass shrimp *Palaemonetes pugio* at a nominal concentration of 10 and 100 ppm. Six of the drilling muds produced 30 to 60 percent mortality in 96 hours at a nominal concentration of 1,000 ppm (Table 34). One mud (#XVIII) produced 100 percent mortality.

Inspection of Tables 4 and 34 gives some clues as to the apparent source of the toxicity of some of the mud samples. Sample #I contained primarily barite, bentonite clay, caustic soda, soda ash and lignite, with small amounts of SAPP, emulsifier and surfactant. Mud pH was 8.7. Only surfactant and SAPP are considered at all toxic, so toxicity of this sample is unexplained. Samples VIII and IX contained significant amounts of ferrochrome lignosulfonate, sodium chromate, sodium bichromate, and oil which may have contributed to their toxicity. SAPP concentration also was high. Sample XIII was heavily treated with ferrochrome lignosulfonate/sodium bichromate mixture (IMCO RD-111). Samples XVII and XVIII were even more heavily treated with ferrochrome lignosulfonate and inorganic chromate salts. In the six days prior to collection of sample XVIII, 7,200 lbs ferrochrome lignosulfonate, 3,400 lbs sodium chromate, and 5,100 lbs

Table 34. Characteristics of used drilling muds from different depths of an exploratory drilling operation in Mobile Bay, Alabama[1] and acute toxicity (measured as percent mortality at 96 hours at a nominal concentration of 1,000 ppm) of the whole muds to intermolt grass shrimp *Palaemonetes pugio* (Data from Conklin et. al., 1980; Jones, 1980; Shokes, personal communication; Gilbert, personal communication).

Sample No.	Date of Collection	(ft.) Depth Interval (see Table 4)	Specific Gravity at 20°C	Total Cr (μg/g dry wt.)	Total Petroleum Hydrocarbons (mg/ℓ)	Toxicity
I	I-31-79	4,600	1.205	55.0		60
II	II-13-79	5,900	1.132	52.4	63.4	0
III	III-6-79	5,974	1.175	41.4	468	5
IV	III-12-79	6,814	1.135	35.4		15
V	III-20-79	8,698	1.155	47.8		0
VI	IV-10-79	12,465	1.139	472		0
VII	IV-24-79	14,423	1.189	662	1,073	5
VIII	V-15-79	14,607	1.244	1,450		30
IX	V-29-79	14,657	1.161	1,810	1,142	50
X	VI-6-79	14,598	1.146	1,590		5
XI	VI-19-79	15,100	1.165	3,750		30
XII	VII-5-79	16,230	1.222	3,250		0
XIII	VII-18-79	17,376	1.279	2,550		30
XIV	VII-24-79	18,023	1.322	2,200		0
XV	VIII-7-79	19,075	1.320	2,290		0
XVI	IX-4-79	20,459	1.738	1,420	1,488	0
XVII	IX-24-79	20,715	1.629	3,500		40
XVIII	X-11-79	21,114	1.492	5,420	3,394	100

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1. See last paragraph, page 107.

sulfonated asphaltene lubricant-hole stabilizer (Soltex) were added to the mud system and undoubtedly contributed to the toxicity of mud #XVIII. Sample XVIII also contained more than 3,000 ppm diesel oil, to which grass shrimp are quite sensitive (Tatem et al., 1978). A drilling mud sample collected on November 16, 1979, contained 5,197 ppm total hydrocarbons (Gilbert, personal communication). The very high total chromium concentrations in these muds reflect the extent to which they had been treated to counteract down-hole problems, mainly high temperature.

Molting grass shrimp *Palaemonetes pugio* were more sensitive than intermolt shrimp to the drilling muds. The five most toxic drilling muds had estimated 96-hr. LC50 values of 363 to 739 ppm. Mysid shrimp *Mysidopsis bahia* were even more sensitive. Estimated 96-hr. LC50 for the most toxic mud sample (#XVIII) was 161 ppm. In a forty-two day life-cycle bioassay in which shrimp were exposed to dispersed mud in a flow-through system, estimated LC50 was 50 ppm whole mud. There was 25 percent mortality in 42 days at a nominal drilling mud concentration of 10 ppm. The authors did not indicate whether drilling fluid particulates tended to accumulate in their flow-through exposure system.

Derby and Atema (1981) studied the effects of two of the Mobile Bay drilling muds (possibly #X and XVIII, though this cannot be ascertained with certainty) on primary chemosensory neurons in walking legs of the lobster *Homarus americanus*. Exposure for 3-5 minutes to seawater suspensions of drilling mud at nominal concentrations of 10 and 100 mg/liter (ppm) interferred with responses to food odors in 29 and 44 percent, respectively, of the chemosensors examined. Groups of lobsters were exposed to a 1 to 10 mm layer of drilling mud over natural sediment in aquaria for 4 to 8 days. Chemoreceptors on the legs of these lobsters were still able to respond to feeding stimuli, though percent of chemosensors responding was lower than among unexposed controls. The authors mentioned unpublished data indicating that feeding behavior was suppressed or abnormal in lobsters exposed to a 1-mm layer of drilling mud in a flow-through exposure system.

Crawford and Gates (1981) described the effects of one of the Mobile Bay drilling muds (collected shortly after sample #XI) on embryonic development of the killifish *Fundulus heteroclitus* and the sand dollar *Echinarachnius parma*. Early development of *F. heteroclitus* was unaffected by concentrations up to 100 ppm mud, measured as dry solids (This corresponds to about 382 ppm whole mud.). At 1,000 and 10,000 ppm (3,816 and 38,160 ppm whole mud) rate of development was slowed, and at 10,000 ppm it was completely arrested. Heart beat rate of 14-32 day embryos was slowed by exposure to 1,000 and 10,000 ppm mud solids. Percent hatching success was decreased at concentrations of 100 ppm and higher mud solids.

Sand dollar *E. parma* larvae developed normally at drilling fluid concentions up to 100 ppm mud solids. At 1000 ppm, development was delayed and percent of plutei were abnormal. Sand dollar eggs treated with 1,000 or 10,000 ppm drilling mud had a low fertilization rate. Sperm were unaffected by drilling mud treatment.

It is quite apparent that several of the used drilling muds from the exploratory drilling operation in Mobile Bay, Alabama are quite toxic to marine animals. Concentrations of these muds (particularly sample XVIII) producing toxic or sublethal responses in sensitive species, life stages and biological process of marine organisms are the lowest reported to date. Because these muds were not intended for ocean disposal, it is difficult to interpret the results in a proper environmental perspective. Some of the drilling muds (especially the first 5) used in Mobile Bay are very similar to drilling fluids which have been permitted elsewhere for ocean disposal. Others are not.

Several other investigators have studied effects of other used drilling muds on growth and developmental parameters in marine animals. Concentrations of 30 percent MAF (30,000 ppm mud added) or greater of used seawater chrome-lignosulfonate drilling mud were acutely toxic to embryos of the killifish *Fundulus heteroclitus* (Neff, 1980; Table 35). Most mortalities took place during the first three days of development or at the time of hatching. Hatching success was decreased significantly at MAF concentrations of 10 percent (10,000 ppm) and higher. Newly hatched fry were extremely tolerant to the MAF. There was a dose-dependent increase in the incidence of developmental abnormalities in drilling mud-exposed embryos. MAF-exposed embryos had a lower heart beat rate and were shorter but heavier than controls at hatching. Percent total hatch of fish embryos was decreased at all MAF concentrations examined.

Carr et al. (1980) reported that when early juveniles of mysid shrimp *Mysidopsis almyra* were exposed continuously to 10-30 percent MAF (10,000-30,000 ppm mud added) of used seawater chrome-lignosulfonate drilling fluid, there was a significant decrease in food assimilation and net growth efficiency, resulting in a reduction in growth rate. However, continuous exposure of larvae of grass shrimp *Palaemonetes pugio* for the duration of larval development to the mud aqueous fraction of mid-weight and high weight lignosulfonate drilling muds had no significant effect on development rate at concentrations that were not lethal (Neff, 1980). Concentrations of 10-15 percent MAF (10,000 - 15,000 ppm mud added) produced mortalities significantly higher than among controls.

Shell growth of spat of the oyster *Crassostrea gigas* was decreased slightly but significantly during continuous exposure for six weeks to 5-20 percent MAF (5,000-20,000 ppm mud added) of mid-weight and high weight lignosulfonate drilling fluids (Neff, 1980). Condition index (ratio of dry meat weight to dry shell weight) of surviving oysters was significantly lower among oysters

Table 35. Summary of the effects of the MAF of used seawater chrome-lignosulfonate drilling mud on the early life history of *Fundulus heteroclitus* (From Neff, 1980).

Parameter	Mud Aqueous Fraction (ppm mud added)						
	0	10,000	20,000	30,000	50,000	75,000	10,000
% 96-hr. survival (4-8 cell stage)	96	97	88	79	54	37	0
% 96-hr. survival (1 day fry)	100	-	100	-	100	-	100
% of survivors expressing growth anomalies at day 16	3.2	27.1	63.3	76.9	93.1	100	--
Heart rate at day 15 (beats per minute)	136.7	121.5	106.2	102.3	88.9	--	--
Day of first hatch	15	17	26	30	--	--	--
% total hatch	89	63	3	1	--	--	--
Total length at hatch (mm)	6.2	5.7	5.4	--	--	--	--
Dry weight at hatch (mg)	0.44356	0.46541	0.5789	--	--	--	--
Chromium concentration in fry exposed continuously (ppm)	0.08-0.09	--	--	--	--	--	0.07-0.09

exposed to 5,000 ppm or higher concentrations of high weight lignosulfonate drilling mud MAF than among controls.

In mussels *Mytilus edulis* exposed for 96 hours to the MAF (33-100 percent equivalent to 33,000 - 100,000 ppm mud added) of three used chrome lignosulfonate drilling muds, there was a tendency, not always statistically significant, for filtration rate to be decreased, respiration rate to be increased and nitrogen excretion rate to be increased (Gerber et al., 1980). When mussels were exposed to a suspended solids phase preparation of low density lignosulfonate mud at a nominal suspended solids concentration of 50 mg/l (corresponding to about 250 ppm whole mud, assuming a total suspended solids concentration in the mud of about 20% by volume) for up to 30 days, shell growth rate was significantly depressed after 10 days. Maximum growth rate depression relative to controls was 54 percent between 10 and 20 days. Low concentrations of suspended particulates (up to 20 mg/ℓ silt) stimulate ingestion rate, assimilation efficiency and growth rate of *M. edulis* (Kiorboe et al., 1980, 1981). However, higher concentrations may interfere with feeding efficiency and thereby decrease growth rate.

Young scallops *Placopecten magellanicus* were more sensitive (Gerber et al., 1981). When exposed continuously to the suspended solids phase preparation of used mid-weight lignosulfonate drilling fluid for 40 days, growth rate of the shells was reduced by 19 to 80 percent in comparison to control rate (Table 36). Estimated total suspended solids concentration in the SSP preparation was 8.9 mg/ℓ (about 49.4 ppm mud added). Growth rate of small scallops was more severely affected than that of larger animals. Growth inhibition was probably due to interference by high suspended particulate concentrations with feeding and assimilation efficiency. In experiments with the MAF of the same mud, intermolt duration for larval stages of lobsters *Homarus americanus* was increased by about 3 days at a concentration of 2% MAF (2,000 ppm mud added).

Table 36. Shell growth rate (mm/10 days) of the ocean scallop, *Placopectin magellanicus*, exposed for 40 days to the total suspended solids phase (SSP) of a medium-density lignosulfonate drilling mud at 8.6 mg/ℓ in a flow-through bioassay. Temperature increased from 5°C to 11.5°C over the exposure period. Each size class was represented by six or seven scallops (From Gerber et al., 1981).

SIZE CLASSES (mm)	GROWTH RATE (mm/10 days)					
	Day 0 to Day 10			Day 11 to Day 40		
	Controls	Exposed	Percent Rate Reduction	Controls	Exposed	Percent Rate Reduction
75.0-80.0	0.15±0.04	(0.09)*	(40.0)*	0.23±0.03	(0.14)*	(39.1)*
70.0-74.9	0.14±0.03	0.08±0.02	42.9	0.17±0.03	0.13±0.04	23.5
65.0-69.9	0.10±0.04	0.08±0.03	20.0	0.16±0.04	0.13±0.05	18.8
60.0-64.9	0.11±0.02	0.06±0.03	45.4	0.14±0.04	0.09±0.03	35.7
55.0-59.9	-0.08±0.06	0.04±0.01	?	(0.07±0.02)	0.10±0.03	?
50.0-54.9	0.10±0.03	0.05±0.01	50.0	0.13±0.03	0.08±0.02	38.5
45.0-49.9	0.08±0.03	0.05±0.02	37.5	0.11±0.04	0.06±0.03	45.5
40.0-44.9	0.10±0.04	0.04±0.00	60.0	0.15±0.02	0.05±0.01	66.7
34.0-39.9	(0.07)*	(0.03)*	(57.0)*	(0.10)*	(0.04)*	(60.0)*
29.0-33.9	0.10±0.04	0.02±0.00	80.0	0.13±0.03	0.04±0.02	69.2
25.0-28.9	0.05±0.02	(0.016)*	(68.0)*	0.08±0.03	(0.02)*	(75.0)*

*These values were estimated from the linear regressions presented in Figure 1 of this report.

Gerber et al. (1980, 1981) examined changes in activity of two key enzymes involved in energy metabolism as indicators of sublethal stress in drilling fluid-exposed marine animals. Activity of enzymes, aspartate aminotransferase (AAT) and glucose-6-phosphate dehydrogenase (G6PdH), were either elevated or depressed in some tissues of exposed animals (Table 37 and 38). Minimum concentrations of drilling mud, either as a whole mud substrate or as a MAF, eliciting responses were in the range of 16-33 percent.

Houghton et al. (1980a) reported that exposure of coonstripe shrimp *Pandalus hypsinotus* to 100,000-150,000 ppm suspensions and pink salmon fry *Oncorhynchus gorbuscha* to a 30,000 ppm suspension of whole used high weight lignosulfonate drilling mud had profound histopathological effects on the gill. Exposure to the drilling mud induced necrosis of the respiratory epithelium and hyperplastic changes in certain cell types. Debris accumulated within interlamellar areas. A concentration of 1,000 ppm drilling mud was without effect.

Thompson and Bright (1977) studied the ability of three reef corals, *Diploria strigosa, Montastrea cavernosa* and *Montastrea annularis*, from the East Flower Garden reef off the Texas-Louisiana coast to clear themselves of a layer of used chrome-lignosulfonate drilling mud. Twenty-five ml of a 1:1 seawater:drilling mud slurry was applied to each coral colony. None of the corals were able to clear their surfaces of this heavy application of drilling mud.

In subsequent experiments, seven species of reef corals were exposed for 96 hours to suspensions of a whole used freshwater ferrochrome lignosulfonate drilling mud in aquaria maintained in 2-3 meters of water on a sand flat at Carysfort Reef off Key Largo, Florida (Thompson and Bright, 1980; Thompson et al., 1980). Three species, *Montastrea annularis, Agaricia agaricites* and *Acropora cervicornis*, were killed by exposure to 1,000 ppm

Table 37. Enzyme activities in the sand shrimp *Crangon septemspinosa*, the green crab *Carcinus maenus*, and the American lobster *Homarus americanus* exposed for 96 hours for the mud aqueous fraction (MAF) of a used light-density lignosulfonate drilling mud. Activity units are mean values in 0.001/min/mg protein ± one standard deviation; four to six animals were combined for analysis. Values for exposure concentrations of MAF are ppm mud added. AAT = aspartate aminotransferase; G6PdH = glucose-6-phosphate dehydrogenase; BDL = below detection limits; S = level of significance where $P < 0.05$, Student's t-test, values inside brackets are not significantly different from controls (From Gerber et al., 1980).

	Sand Shrimp T° = 18C		Green Crabs T° = 8C		Am. Lobster* T° = 12C	
Exposure Concentration	AAT	G6PdH	AAT	G6PdH	AAT	G6PdH
0	BDL	0.13±0.05	BDL	0.04±0.07	7.13±0.40	5.92±0.70
10,000		S		S	8.65±0.61 S	2.77±0.49 S
33,000	BDL	0.01±0.01	BDL	0.18±0.06		1.39±0.29
66,000	BDL	0.05±0.04	BDL	0.33±0.10		
100,000	BDL	0.05±0.02	BDL	1.03±0.14	12.44±0.72	0.16±0.05
		$r^2=0.26$		$r^2=0.84$	$r^2=0.96$	$r^2=0.69$

* Activity is based on the heart tissue.

Table 38. Enzyme activities* of the heart tissue of the northern crab *Cancer borealis* exposed to the whole mud fraction and the mud aqueous fraction of a medium-density lignosulfonate mud for 96 hours at 5°C (From Gerber et al., 1981).

Exposure Concentration (%)	Whole Mud		Mud Aqueous Fraction	
	AAT	G6PdH	AAT	G6PdH
0	4.33 ± 0.79	0.09 ± 0.04	5.02 ± 0.94	0.12 ± 0.05
16	7.77 ± 1.10	0.15 ± 0.06	-	-
33	9.35 ± 1.64	0.27 ± 0.12	9.20 ± 1.34	0.18 ± 0.05
66	13.34 ± 0.97	0.36 ± 0.16	11.67 ± 1.72	0.25 ± 0.09
100	21.02 ± 1.88	0.74 ± 0.23	17.35 ± 1.64	0.62 ± 0.16
	r^2 = 0.98	r^2 = 0.94	r^2 = 0.98	r^2 = 0.82

AAT = aspartate aminotransferase, G6PdH = glucose-6-phosphate dehydrogenase, BDL = below detectable levels.

*Activity units are the mean values of five replicate analyses ± one standard deviation of the mean in 0.001/min/mg protein.

whole drilling mud. At a nominal concentration of 100 ppm, these species as well as *Porites furcata* and *P. astreoides* had a statistically significantly higher percent polyp retraction than control colonies. A nominal drilling mud concentration of 316 ppm was required to significantly increase percent polyp retraction in *Porites divaricata*. Polyps of *Dichocoenia stokesii* did not respond to any drilling mud concentration.

Krone and Biggs (1980) studied the effect of a suspension of 100 ppm of a used drilling mud from Mobile Bay, Alabama (collected about the same time as sample III; Table 34), alone or spiked with 3 or 10 ppm ferrochrome lignosulfonate on oxygen consumption and ammonium excretion in the coral *Madracis decactis*. Respiration and excretion rates of corals exposed to 100 ppm drilling mud alone were not markedly different from those of controls. Corals exposed to the ferrochrome lignosulfonate-spiked drilling mud had elevated rates of respiration and excretion during the first week of exposure. Much of the difference was due to extreme responses of a few colonies which later became moribund. The high degree of variability and small sample size per treatment (n = 4) make it difficult to interpret the results. In addition, it is unlikely that the ferrochrome lignosulfonate added to the drilling mud would be in the same physical/chemical form as that in an authentic used ferrochrome lignosulfonate drilling mud.

Small colonies of *Montastrea annularis* attached to cement tiles were placed on the Carysfort Reef in 3 meters of water (Hudson and Robin, 1980a,b). A 2-4 mm layer of freshly prepared freshwater ferrochrome lignosulfonate drilling mud was applied to the colonies 4 times at 2.5-hour intervals. The corals were recovered 6 months later and growth rate was measured by X-ray radiography. Growth rates of drilling mud-treated corals were slightly lower and less variable than rates of control corals.

It can be seen from the results discussed above, that in a majority of cases, significant deleterious sublethal repsonses in marine animals are observed at drilling fluid concentrations only slightly lower than those which are acutely toxic. In the most sensitive species and life stages, such as juvenile ocean scallops, lobster larvae, some reef corals, and mysid shrimp, deleterious sublethal responses are observed during chronic exposure to whole suspended drilling mud concentrations in the 50-100 ppm range. These species and life stages appear to be very intolerant to prolonged exposure to high suspended particulate concentrations. Damage is probably caused by abrasion or clogging of delicate gill and gut epithelial surfaces.

Microcosm Studies

Various types of experimental microcosms have become popular in recent years as links between laboratory experiments and field observations. Microcosms have been used a few times to study the possible effect of drilling fluids on marine benthic communities. Most of the marine invertebrates that spend their adult lives on or in the bottom sediments have early life stages (larvae) that float in the water column (are planktonic). When the larval forms approach the time of metamorphosis, they seek out a suitable type of substrate and are transformed into adult form. Since the adults usually have only limited locomotory ability, the planktonic larva is the main mechanism of species dispersal and of recruitment each year of new animals to benthic habitats. If drilling muds deposited on or in natural substrates are toxic or change sediment texture significantly, they might prevent some species from settling, changing the composition of the benthic community. Tagatz et al. (1978, 1980) studied the effects of a used lignosulfonate drilling mud, applied as a layer over clean sand substrate or mixed with the sand, on recruitment of larvae to the substrate. Natural unfiltered seawater flowed through aquaria containing the substrates.

Recruitment of annelids and coelenterates was lower in aquaria containing drilling fluid than in control aquaria (Table 39). Recruitment of arthropods was diminished significantly only in aquaria containing a layer of 0.2 cm drilling fluid on the sand substrate. Mollusc recruitment was unaffected. Total number of animals recruited to drilling mud-treated aquaria was significantly lower than the number recruited to control aquaria. Among the most severely affected group, the annelids, most of the decrease in numbers of individuals in drilling mud-containing aquaria was due to decrease in abundance of one species, *Armandia maculata*, which was very abundant in the control aquaria. Number of species of annelids present was unaffected at a concentration of 1 part mud to 10 parts sand, and dropped by a mean of about two species per aquarium at higher exposure concentrations. Concentrations required to elicit these responses were rather high; mud/sand mixtures of 1:10 and 1:5 (100,000 and 200,000 ppm drilling mud) or a layer of 2-mm mud on the sand.

Rubinstein et al. (1980) made similar observations in their studies of the chronic toxicity of the controversial Mobile Bay used drilling muds. In this case, molluscs were most severely affected. Numbers were greatly diminished at a nominal 100 ppm drilling mud but their abundance was greater than that in the control aquaria at nominal 10 and 30 ppm mud concentrations. Polychaete worm and crustacean recruitment was affected only at the highest mud concentration (100 ppm). It should be recalled that at this nominal concentration in the flow-through system, a layer of more than 10-mm drilling fluid particulates accumulated on the surface of the substrate during the 100-day timecourse of this experiment. This undoubtedly influenced settling and survival of larvae. In the two investigations just summarized, the clean natural substrate examined was sand. Since drilling fluids consist primarily

Table 39. Numbers of animals and species (mean no. per aquarium) collected from aquaria containing sand alone or sand-chrome lignosulfonate drilling mud mixtures and receiving unfiltered natural seawater at a flow rate of 200 ml/min for 8 weeks (From Tagatz et al., 1978, 1980).

	Number of individuals or species (in brackets)			
Taxon	Control	Mud 1:10	Mud 1:5	2-mm Mud Cover
Annelida	276(7.8)	174*(7.9)	106*(5.8*)	77*(5.1*)
Armandia maculata	126	55	39	3
Mediomastus californiensis	41	21	7	19
Mollusca	53(3.0)	39(3.0)	41(2.9)	27(1.8)
Acteocina canaliculata	23	16	19	17
Laevocardium mortoni	16	7	5	4
Arthropoda	36(1.8)	28(2.1)	44(1.9)	11*(0.8*)
Corophium acherusicum	26	14	29	5
Coelenterata	58(0.8)	13*(0.2)	23*(.2)	4*(0.4)
Aiptasia pallida	58	13	23	4
Other Phyla	6(0.2)	4(0.1)	5(0.1)	0(0)
Total	429(13.5)	258*(13.8)	219*(11.1)	119*(8.0*)

*, significantly less than control at 5% level; significance is indicated only for phyla.

of clay-sized particulate material, mixtures of drilling mud and sand have a different texture than sand alone. It is well-established that sediment texture is a critical factor controlling choice of a suitable substrate by planktonic larvae (Thorson, 1957, 1966). Thus, the responses observed could be due to toxic effects of drilling mud or to changes in sediment texture. Since some species prefer finer textured sediments, it is not surprising to sometimes find a species more abundant in or restricted to the drilling mud-containing sediment. So the effect of the admixture of large amounts of drilling fluid with coarser natural sediments might be to change species composition of benthic fauna in the affected area.

Gilfillan et al. (1981) took a slightly different approach. Trays containing azoic (organism-free) mixtures of 0%, 33%, 66% and 100% of a used high weight lignosulfonate drilling mud, seawater-washed drilling mud, and fine natural mud (similar in texture to the drilling fluid), were placed on a soft bottom in 2.5 m of water in a Maine estuary for 84 days. Washing of drilling mud removes the soluble materials and fine, low density particulates, leaving a settleable fraction that resembles the fraction of drilling mud most likely to accumulate on the bottom below the mud discharge pipe. After 84 days, animal communities found in trays containing drilling mud were slightly more diverse than those in trays containing no drilling mud. However, population density was much lower in trays containing 66 and 100 percent whole or washed drilling fluid. The authors concluded that as much as 33 percent of either whole or washed drilling fluid could be incorporated into the sediment used with no reduction in population density and only a slight change in diversity. Thus, it would appear that changes in sediment texture must be considered in evaluating results of studies of this sort.

Interpretation of Bioassays in Relation to Field Observations

The results reported above show that for the majority of used offshore drilling muds examined to date, concentrations lower than 10,000 ppm mud added (greater than 100 to 1 dilution) are not likely to cause serious acute damage to marine organisms. Sublethal or chronic effects are sometimes seen in sensitive species at 50-1,000 ppm whole mud. A mud dilution of 20,000 to 1 would render such muds nontoxic. During a high rate bulk discharge of drilling mud at a rate of 1000 bbl/hr from an exploratory platform in the Gulf of Mexico, the 20,000 to 1 dilution of drilling mud was reached about 150 meters downcurrent from the discharge (Ayers et al., 1980b).

It is extremely unlikely that any organisms in the water column in the vicinity of a mud discharge will actually be exposed continuously to high concentrations of drilling mud for 96 hours (the length of time used in most acute bioassays) and certainly not for 40-100 days (the length of some chronic effects studies). As discussed above, during drilling, drilling mud and cuttings are discharged intermittently and at highly variable rates. They are diluted and dispersed in the water column rapidly.

However, there could be a localized impact of drilling mud discharge on benthic organisms and communities directly under and downcurrent from the discharge where drilling mud and cuttings solids settle out. Changes may be qualitative (species composition) rather than quantitative and may be only temporary (months at most).

Field Studies

The few field studies published to date on effects of drilling mud discharges on demersal, benthic and biofouling communities around offshore exploratory and production platforms tend to corroborate conclusions derived from laboratory studies; that ecosystem effects of drilling mud discharge to the ocean are minimal and when detected are of short duration.

Zingula (1975) reported that motile organisms were active on the surface of cuttings piles under oil rigs even while drilling was still going on. He suggested that colonizing organisms were able to rework the pile and turn it into "normal" sea bottom within a few months.

Gettleson (1978) monitored health of reef corals on the East Flower Garden Bank off the Texas-Louisiana coast before, during, and after drilling of an exploratory well approximately 2,100 meters to the southeast of the reef. Although some of the discharged mud and cuttings were distributed by currents to a distance greater than 1,000 meters from the rig, none could be detected in the coral reef zone. The drilling operation had no observable effect on the coral reef.

Lees and Houghton (1980) studied benthic communities in the vicinity of the Lower Cook Inlet, Alaska, C.O.S.T. well before, during and after the drilling operation. Some changes in benthic communities were seen near the drilling platform during the course of the study. However, no statistically significant differences could be attributed to effects of drilling operations because of patchiness in faunal distribution, probably due to differences in successional stages between areas sampled. They concluded that rates of accumulation of drilling mud and cuttings on the bottom were not great enough in the dynamic high-energy environment of Lower Cook Inlet to measureably affect the benthic populations.

In a related study of the same drilling rig, Houghton et al. (1980a) placed pink salmon fry, shrimp, and hermit crabs in live boxes at 100, 200, and 1,000 meters downcurrent from the mud discharge. After four days, there were no mortalities that could be attributed to the mud discharge plume.

Menzie et al. (1980) studied the short-term effects of drilling mud and cuttings discharges on benthic communities around an exploratory drilling platform in the Mid-Atlantic outer continental shelf off Atlantic City, New Jersey. A zone of visible drilling discharge accumulations (primarily natural clays) was observed in the immediate vicinity of the well site, while elevated levels of clays were detected up to 800 m southwest of the site. Fish and crab abundance increased substantially between the predrilling and postdrilling surveys in the immediate vicinity and to the south of the well site. These animals may have been attracted to the region by the increased microrelief afforded by the cuttings accumulations. The cuttings had no apparent effect on abundance of the sand star *Astropecten americanus* which was the most abundant megabenthic species. In fact, large numbers of sand stars congregated near the well site, apparently attracted by mussels *Mytilus edulis* that had fallen from the drilling rig and anchor chains.

Within about 150 m of the discharge, sessile benthic animals like pennatulid coelenterates (sea feathers) were subject to burial by drill cuttings. However, within this zone there were patches of high abundance of macrobenthos.

Beyond the immediate vicinity of the discharge site, reduction in abundance of macrobenthic organisms was attributed in part to increased predation by fish and crabs and in part to increased clay content of the sediments. No correlation was observed between abundance of macrobenthic organisms and barium content of sediments or animal tissues. The affected areas extended to the southwest of the well site for up to 800 m, in the direction of the prevailing currents. The authors concluded that conditions in the benthos should return to the predrilling state quite rapidly as bottom materials are reworked and resuspended, and as new natural material is deposited.

Benech et al. (1980) studied fouling communities on submerged pontoons of a semisubmersible drilling rig off Southern California. Pontoons within 10 meters downcurrent of the mud/cuttings discharge had different fouling communities than pontoons not exposed to drilling mud. Differences were attributed primarily to mud sedimentation and not to light or exposure. Species of algae sensitive to sedimentation and turbidity were eliminated from the mud-exposed surfaces. With their disappearance, herbivorous invertebrates that feed on them disappeared. Sediment-tolerant species became more abundant on the mud-exposed pontoons. Effects were highly localized.

We can conclude from the results of these publications that impact of mud and cuttings discharge on benthic and fouling communities is related to the amount of material accumulating on the bottom under the discharge pipe, which in turn is related to current speed and related hydrographic factors. In high-energy environments, little mud and cuttings accumulates and impact on the benthos is minimal. In low energy situations, more material accumulates and there may be temporary reductions in abundance of certain benthic species due to burial or incompatibility with clay. Other changes at the well site not associated with mud and cuttings discharges often obscure effects of the discharges. No evidence of chemical toxicity of drilling muds has been observed in the field.

BIOAVAILABILITY OF HEAVY METALS FROM DRILLING MUDS

Laboratory Studies

Water-based drilling muds, which are used in nearly 80% of offshore drilling operations (Ray, 1979), are usually mixtures of clays, inorganic salts and a variety of organic and metaloorganic compounds in fresh or salt water. Metal composition of drilling fluids was discussed earlier in this review. Typical concentrations of several metals in used drilling muds are listed in Table 41 and Appendix I, Tables 2a-9a. Elevated concentrations of barium, chromium, zinc, cadmium, and lead, presumably derived in part from discharged drilling muds, have been reported in the water and bottom sediments in the immediate vicinity of offshore exploratory wells (Ecomar, 1978; Crippen et al., 1980; Gettleson and Laird, 1980; Mariani et al., 1980; Meek and Ray, 1980; Tillery and Thomas, 1980; Wheeler et al., 1980; Trocine et al., 1981). The important question relating to these metals is whether marine animals can accumulate them in their tissues from the water or sediment to concentrations high enough to be toxic to the animals themselves or to higher trophic levels including human consumers of these fishery products.

Bioaccumulation of metals from two samples of barite by two benthic invertebrates, the hard shell clam *Mercenaria mercenaria* and the sand worm *Nereis virens*, was investigated by Espy, Huston and Associates, Inc. (1981). The bioaccumulation test protocol for dredge material was followed (EPA/COE, 1977). The animals were exposed for 10 days to a 1.5-mm layer of barite over 3-mm clean sand in aquaria containing artificial seawater. Copper was the only metal that increased in concentration in the overlying seawater during the exposure period. The increase was very small. Neither species showed a statistically significant accumulation of any of the metals analyzed, zinc, mercury, chromium, lead, cadmium, copper and barium, during the 10-day exposure period. Mean concentrations of copper and barium in polychaetes did seem to rise slightly during exposure to barite. Because of small sample size (n = 3) and variability in metals concentrations in both experimentals and controls, the differences were not statistically significant.

When grass shrimp were exposed to 50 mg/ℓ barite in seawater (mostly as a solid powder), they ingested the particulate barite (Brannon and Rao, 1979). After one week exposure to barite, the shrimp contained whole-body residues of 9,134 mg/kg barium, compared to 26 mg/kg barium in controls. Most of this was undoubtedly associated with particulate barite in the gut. When shrimp were exposed for 106 days to 500 mg/ℓ barite, barium accumulated in several tissues, particularly the carapace. Exuviae cast off at the time of the molt contained up to 19,987 mg/kg barium, compared to a maximum of 420 mg/kg in exuviae of control shrimp. At the end of 106 days, hepatopancreas and carapace of shrimp contained about 8,000 ppm barium, while muscle tissue contained about 1,000 ppm. Thus, shrimp are able to accumulate barium from solid barite. The barium tends to be sequestered with strontium in the calcium carbonate skeleton. This barium is lost with the old exoskeleton at the time of the molt. Barium is a normal trace component of carbonate skeletal structures in marine invertebrates (Chow and Snyder, 1980). Physiological effects of barium accumulation in the shrimp are unknown.

Liss et al. (1980) studied the concentrations of barium, chromium, iron and lead in used drilling muds, in the liquid (soluble) phase of drilling muds, in seawater suspensions of mud, and in the tissues of the sea scallop *Placopecten magellanicus*. Chromium, iron, and lead concentrations in the liquid phase of whole muds were higher than expected based on the solubility of the respective hydroxides. Concentrations of barium and chromium in solution in seawater suspensions of mud were also higher than expected. These soluble metals apparently were complexed with soluble organic additives, particularly lignosulfonates, in the mud. In scallops exposed for 27 days to 1g/ℓ of a used low density chrome lignosulfonate drilling mud from the Baltimore Canyon, chromium concentration in the kidney rose to nearly 3 ppm, compared to about 1.5 ppm chromium in controls. The slow adductor muscle, the part of the scallop consumed by humans, did not accumulate any chromium. When scallops were exposed to 1g/ℓ of a synthetic attapulgite clay based mud for 28 days, they accumulated up to 100 ppm barium in the kidney. Kidneys of unexposed control animals contained a maximum of about 12 ppm barium. No barium was accumulated in the adductor muscle.

Page et al. (1980) studied the accumulation of chromium from used offshore drilling muds by sand shrimp *Crangon septemspinosus*, sand worms *Nereis virens*, and mussels *Mytilus edulis*. Sand shrimp accumulated nearly 2 ppm chromium in their tissues during exposure for 96 hours to a 50% MAF of used low weight lignosulfonate drilling mud. Nearly all the accumulated chromium was released during 96 hours exposure to clean seawater. Cadmium was not accumulated from the mud by the shrimp. The sand worms failed to accumulate chromium from the MAF or LSP preparations of used high weight lignosulfonate mud. Mussels accumulated approximately 2-4 ppm chromium in their tissues during continuous exposure for 30 days to a suspended solids phase preparation of used low weight lignosulfonate drilling mud containing 0.03 ppm chromium. The mussels did not accumulate cadmium from the MAF of mid-weight lignosulfonate mud and seawater chrome lignosulfonate mud.

Mussels were also exposed to several forms of chromium for up to seven days (Table 40). Chromium in the MAF of the used mid-weight lignosulfonate mud was the form least available for accumulation by the molluscs. Chromium as the inorganic trivalent salt ($Cr\ Cl_3$) was the most readily accumulated followed by chromium associated with ferrochrome lignosulfonate. These results show that complexation of chromium with lignosulfonate decreases its apparent bioavailability to mussels; and association of chrome lignosulfonate with the clay fraction of the mud, as occurs in used chrome lignosulfonate muds (McAtee and Smith, 1969; Knox, 1976; Liss et al., 1980), decreases the bioavailability further.

Carr et al. (1981) examined the bioavailability of chromium from used seawater chrome lignosulfonate drilling mud to three marine crustaceans, *Portunus spinicarpus*, *Penaeus aztecus* and *Palaemonetes pugio*, a polychaete worm, *Nereis virens*, and bivalve mollusc, *Rangia cuneata*. All five species showed an apparent accumulation of chromium during exposure to different types of mud-seawater mixtures. When the crustaceans were returned to mud-free seawater, they rapidly released the accumulated chromium. Clams *R. cuneata* accumulated significant amounts of chromium when they were exposed to a sand

Table 40. Accumulation of chromium by mussels *Mytilus edulis* during exposure to chromium in different forms for seven days (Data from Page et al., 1980).

Exposure Mixture	Cr in Exposure Medium (ppm)	Cr in Mussel Tissues (μg/g dry wt.) (ppm)			
		0 days	1 day	4 days	7 days
Seawater Control	0.1	1.3	0.7	0.3	1.6
MAF of Mid Weight Mud	1.4	1.0	3.7	5.8	6.6
Ferrochrome Lignosulfonate	0.7	1.0	4.1	10.0	12.5
Cr^{+3} solution ($CrCl_3$)	0.6	1.0	36.7	44.3	49.5

substrate containing a layer of drilling mud (Figure 13). However, most of the chromium was released within 24 hours when the clams were returned to clean natural substrate, indicating that much of the chromium accumulated was in the form of unassimilated mud components in the digestive tract or on the gills. Clams and worms both accumulated chromium from the mud aqueous fraction. The worms released the chromium more slowly than the clams did when both were returned to clean seawater.

McCulloch et al. (1980) investigated accumulation of chromium, lead, and zinc from the four used drilling muds, evaluated toxicologically by Gerber et al. (1980, 1981) and Neff et al. (1980, 1981), by marsh clams *Rangia cuneata* and juvenile Pacific oysters *Crassostrea gigas*. Concentrations of several metals in the four muds is summarized in Table 41. As expected, chromium concentrations were high in the three chrome lignosulfonate muds and low in the spud mud. Copper concentrations were high in the MWL and HWL muds and lead and zinc concentrations were unexpectedly high in all four muds.

Clams *Rangia cuneata* accumulated only small amounts of chromium and lead from the mud aqueous fraction of mid-weight lignosulfonate mud. Less than half the accumulated chromium and lead was released in four days when the clams were returned to clean seawater. When juvenile Pacific oysters *Crassostrea gigas* were exposed to the mud aqueous fraction of three drilling muds for two weeks, they showed little or no net accumulation of chromium, lead or zinc. Maximum concentration of chromium accumulated, 7.53 ppm (approximately three times the concentration in control animals), was in oysters exposed to the 40% MAF of mid-weight lignosulfonate drilling mud. Oysters exposed to the 40% MAF of this mud also accumulated slightly more than 2 ppm lead in 14 days. There was no net accumulation of zinc from the MAF of any mud.

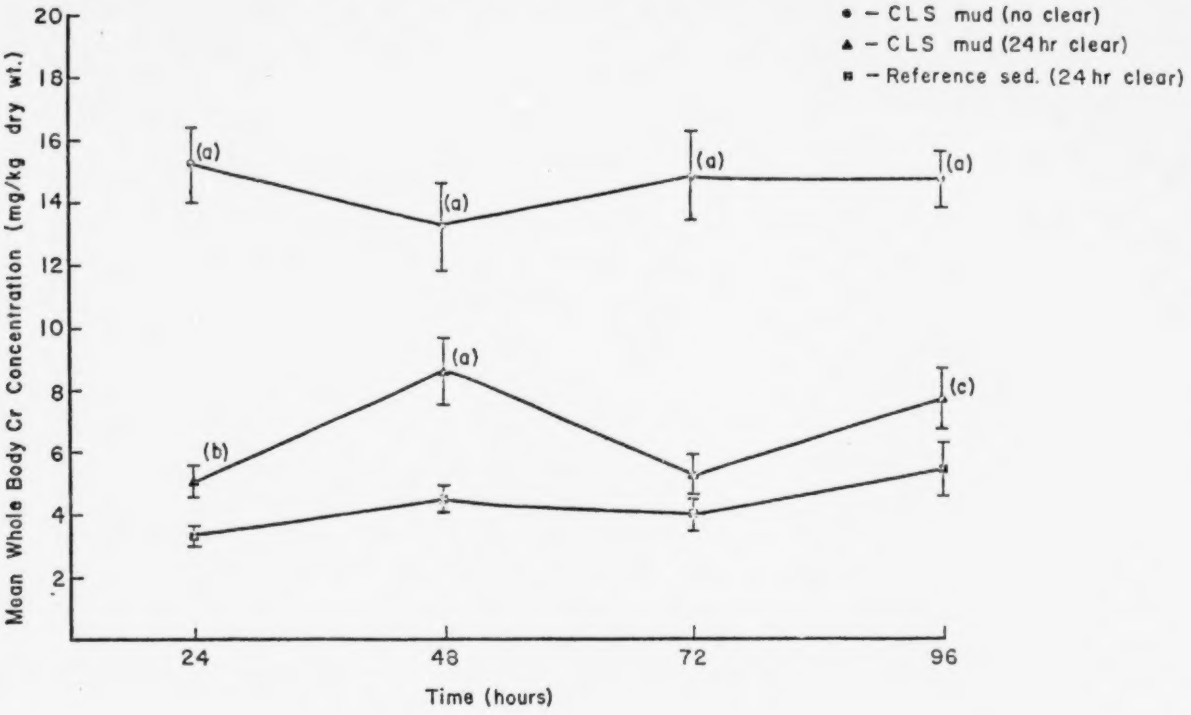

Figure 13. Accumulation of chromium by the marsh clam *Rangia cuneata* during exposure to reference sediment from San Antonio Bay, Texas (containing 20.36 mg Cr/kg dry weight) and to a layered solid phase preparation (LSP; 1:16 drilling mud: seawater) of used seawater chrome lignosulfonate drilling mud (containing 485 mg Cr/kg dry weight) with or without a 24-hour period in clean seawater after exposure. Vertical bars represent standard errors of mean for 10 clams.

a, significantly different from value for clams in reference sediment at corresponding sampling time at $p < 0.005$.

b. significantly different from corresponding reference sample at $p < 0.025$.

c, significantly different from corresponding reference sample at $p < 0.05$ (From McCulloch et al., 1980).

Table 41. Concentrations of several metals in four used drilling muds as determined by flame atomic absorption spectrophotometry. All concentrations are in mg metal/kg dry mud (ppm), and standard deviation of two replicate analyses. Values in parentheses are concentrations determined by argon plasma emission spectrophotometry (From McCulloch et al., 1980).

Mud	Drilling Mud[1]			
	CLS	MWL	HWL	Spud
Cadmium	3.0±0.7 (1.20)	19.2±1.5 (15.86)	10.9±3.5 (3.04)	3.5±1.5 (7.23)
Chromium	485.2±4.4 (395.0)	416.7±8.5 (473.0)	224.9±3.5 (287.0)	10.9±0.5 (70.90)
Copper	48.2±7.9	127.0±8.5	118.8±8.4	30.2±3.3
Lead	179.4±27.8 (68.57)	915.3±45.7 (477.0)	209.5±13.8 (124.6)	134.2±20.9 (81.70)
Zinc	251.4±52.8	604.8±13.1	274.5±35.4	297.3±1.6

1, CLS, seawater chrome lignosulfonate mud; MWL, mid-weight lignosulfonate mud; HWL, high weight lignosulfonate mud; Spud, spud mud.

Rubinstein et al. (1980) reported elevated concentrations of barium, chromium and lead in tissues of oysters following exposure for 100 days to nominal concentrations of 10 to 100 ppm of the controversial drilling muds from Mobile Bay, alluded to earlier. Mean concentrations of barium, chromium, and lead in the drilling muds tested were 1,086, 1,372, and 41 μg/g (ppm), respectively. One sample of mud had a chromium concentration of 5,420 ppm. Oysters were placed in clean seawater for several hours before analysis to allow purging of unincorporated mud particulates. Maximum metals concentrations in oysters exposed to 100 ppm drilling mud were 56.17 ppm barium, 9.98 ppm chromium, and 3.26 ppm lead, compared to levels of 1.90 ppm barium, 0.65 ppm chromium, and 1.08 ppm lead in unexposed control oysters. It should be recalled that mud particulates accumulated in the aquaria during exposure, so that actual exposure concentrations were substantially higher than nominal values. Other metals examined, including aluminum, iron and zinc, were not accumulated by the oysters.

Tornberg et al. (1980) studied accumulation of cadmium, chromium, lead, and zinc by amphipods (*Onisimus* sp. and *Boeckosimus* sp.) during exposure for up to 20 days to several dilutions of XC-polymer drilling fluids (heavy metal composition summarized in Appendix I, Table 9a). Fifty animals were pooled per sample and coefficients of variation between replicates were high. Mean metal concentrations in control amphipods were 0.3 ppm (μg/g dry wt.) cadmium, 3.0 ppm chromium, 9.7 ppm lead and 85.8 ppm zinc. Metals accumulation was neither dose nor time dependent. Maximum metal accumulation by the crustaceans was approxiamtely 1.7 ppm cadmium, 5.3 ppm chromium, 20 ppm lead, and 140 ppm zinc. So, in this case the greatest relative accumulation (nearly 6-fold) was of cadmium. The other metals were accumulated 2-fold or less in 20 days.

Gerber et al. (1981) studied accumulation of chromium by the ocean scallop *Placopecten magellanicus* during exposure for 40 days to a suspended solids phase (SSP) preparation or for 7 days to the mud aqueous fraction (MAF) of a mid-weight lignosulfonate drilling mud (Table 42). Scallops exposed to the SSP for 40 days contained about twice as much chromium as was present in tissues of control animals. Accumulation of chromium by scallops exposed to the MAF was dose-dependent. Maximum accumulation was to about three times the concentration in control scallops. Scallops accumulated more chromium more rapidly from a 2% MAF than from an 8.6 mg/ℓ total suspended solids SSP preparation, both of which contained the same concentration of chromium in the aqueous phase.

These studies show that heavy metals associated with used drilling muds have a limited bioavailability to marine animals. Chromium appears to be the most readily accumulated of the mud-associated metals. Most of the chromium in used drilling mud is associated with the high molecular weight lignosulfonate fraction and with the clay. Organically bound and particle-absorbed heavy metals usually are much less bioavailable than the metal ion in solution. Much of the lead, zinc and possibly cadmium is in particulate form associated with pipe dope (usually high in lead and zinc) and the clay or barite fractions of the mud (McCulloch et al., 1980; Kramer et al., 1980). Such tightly bound metals generally cannot be assimilated by marine animals. These particulate metals may be taken up from the digestive tract by phagocytosis (George et al., 1976; Conklin et al., 1980). The metals are retained in intracellular vacuoles and remain in particulate form. They may eventually be transferred to the kidney and excreted. This may explain the observation of Liss et al. (1980) that chromium and barium from drilling muds are accumulated in the kidney but not the edible muscle of the sea scallop. The available evidence indicates that there is little likelihood that heavy metals would be accumulated from

Table 42. Bioaccumulation of chromium by the ocean scallop, *Placopecten magellanicus*, exposed for 40 days to the suspended solids phase (SSP) and for 7 days to the mud aqueous fraction (MAF) of a medium density lignosulfonate drilling mud (From Gerber et al., 1981).

	Concentration of Chromium ppm/g dry wt.	
	In Solution	In Tissues*
SSP		
Control Tank	0.074	1.20
8.6 mg/liter suspended solids	0.093	2.41
MAF		
Control Tank	0.065	1.26
0.5%	0.084	1.90
2.0%	0.093	3.30
8.0%	0.112	3.70
33.0%	0.244	3.94

*Whole animals were ground and analyzed.

environmentally realistic levels of used drilling muds in edible portions of shell and finfish to concentrations that would pose a health hazard to human consumers of such fishery products.

Field Studies

As indicated above, elevated concentrations of several metals have been reported in the immediate vicinity of drilling platforms in the water column during drilling fluid discharges and in bottom sediments following mud and cuttings discharge. Heavy metals concentrations in the water column reach background very quickly and within a short distance of the mud discharge pipe. As discussed earlier, Ray and Meek (1980) estimated that trace metal concentrations reached background in the discharge plume within 200 meters of the discharge pipe during mud discharge from a platform on Tanner Bank, California. Ayers et al. (1980b) estimated that, in the drilling mud plume from a platform in the Gulf of Mexico, trace metal concentrations reached background levels about 500 meters from the discharge source during a 275 bbl/hr. discharge and about 1,000 meters from the discharge source during a 1,000 bbl/hr. test. Even at the highest discharge rates, suspended solids concentrations reached background levels within 100 minutes. Thus, potential for accumulation of toxic metals from drilling muds by water column organisms is minimal.

Several drilling mud associated metals tend to accumulate in bottom sediments in the immediate vicinity and downcurrent of the drilling rig, where they may persist indefinitely (Crippen et al., 1980; Gettleson and Laird, 1980; Mariani et al., 1980; Meek and Ray, 1980; Tillery and Thomas, 1980; Wheeler et al., 1980; Trocine et al., 1981). Thus, the important question becomes: What is the bioavailability of these sedimented metals to benthic marine animals?

Mariani et al. (1980) studied changes in concentrations of several metals in sediments and benthic invertebrates in the vicinity of an offshore exploratory rig in the Baltimore Canyon off New Jersey before and after drilling. Elevations in only barium concentration in the postdrilling sediment samples could be attributed to mud and cuttings discharges. Other investigators have identified barium as the major metal accumulating in bottom sediments around drilling mud discharges (Chow and Snyder, 1980; Gettleson and Laird, 1980; Wheeler et al., 1980). This is not surprising considering the high density and low solubility of barite and the large amounts used in most deep hole muds.

Mixed species assemblages of brittle stars, molluscs, and polychaetes collected during the postdrilling survey, approximately two weeks after drilling-related operations were terminated, had significantly elevated concentrations of barium and mercury in comparison to animals collected in the predrilling survey nearly a year earlier. The increase in mercury concentration in the animals was unexplained. Mercury concentrations in the discharged drilling muds and bottom sediments were below the limit of detection (<0.05 ppm) (Ayers et al., 1980a). The greatest apparent accumulation of mercury was by the molluscs. Mariani et al. (1980) reported that predrilling mercury concentrations in molluscs ranged from <0.009 to 0.665 ppm, and in postdrilling samples, mercury concentrations ranged from 0.05 to 11.26 ppm. Review by Mariani and associates of the analytical procedures and results revealed computational errors in the postdrilling mercury data (Ayers, personal communication). Recalculated range of mercury concentration in postdrilling mollusc tissue samples was <0.006-0.58 ppm. Revised, corrected values for mercury in postdrilling samples of brittle stars and polychaetes were in the

<0.006 - 0.37 ppm range. So, apparently there was not a statistically significant increase in mercury concentration between pre- and postdrilling biota samples.

Concentration gradients of barium in benthic organisms were not correlated with concentration gradients in bottom sediments. Polychaete worms had higher concentrations of tissue chromium in postdrilling than in predrilling samples. The other species did not accumulate chromium.

Crippen et al. (1980) measured concentrations of several metals in sediments, drilling muds and benthic animals from a drilling site in the Beaufort Sea. Mercury, lead, zinc, cadmium, and arsenic were present at higher concentration in the drilling mud than in the surface sediment. No correlation was found between metal levels in the sediment near the mud discharge site and levels in benthic infaunal organisms.

Tillery and Thomas (1980) reviewed several investigations of distribution of heavy metals in sediments and biota in oil production fields in the Northwest Gulf of Mexico. They reported concentration gradients of barium, cadmium, chromium, copper, lead and zinc in surficial sediments that decreased with distance from some platforms. Trace metal concentrations in muscle tissues of four commercially important species (brown shrimp *Penaeus aztecus*, Atlantic croaker *Micropogon undulatus*, sheepshead *Archosargus probatocephalus*, and spadefish *Chaetodipterus faber*) generally were not significantly higher in animals from the vicinity of oil production fields than in animals from other regions.

As before, the results of the limited field studies to date tend to corroborate the conclusions of laboratory studies. Accumulation of heavy metals from sedimented drilling muds is very low, when it can be demonstrated at all. Most of the metals of concern are associated with the barite and bentonite clay fractions of the drilling mud (Crippen et al., 1980; Kramer et al., 1980). The exception is chromium, which is associated primarily with lignosulfonate. In a used chrome lignosulfonate drilling mud, much of the chrome lignosulfonate becomes bound to the clay fraction (McAtee and Smith, 1969; Skelly and Dieball, 1969; Knox, 1978). Heavy metals which are in the form of insoluble salts, are adsorbed to particulates, or are complexed with organic solutes, usually have a much lower bioavailability to marine animals than do the metal ions in solution (Jenne and Luoma, 1977; Neff et al., 1978; Breteler et al., 1981). Page et al. (1980) showed that mussels *Mytilus edulis* accumulated more chromium from solution as Cr^{+3} than from solutions of ferrochrome-lignosulfonate or mud aqueous fractions of chrome lignosulfonate drilling mud. Capuzzo and Sasner (1977) showed that chromium adsorbed to bentonite clay was much less bioavailable to mussels *Mytilus edulis* and clams *Mya arenaria* than was an equivalent amount of chromium in solution as $CrCl_3$. Neff et al. (1978) studied the accumulation of heavy metals from metal-contaminated sediments, five species of invertebrates, three salinities, and eight metals, a significant accumulation of a metal was demonstrated only 36 times (26.5%). In many cases where a statistically significant accumulation of a metal from sediment occurred, the uptake was quantitatively marginal and of doubtful ecological significance. Thus, high levels of a metal in a sediment or drilling mud sample are not by themselves an indication of biological hazard. These adsorbed metals have a very limited bioavailability.

One can conclude that benthic marine animals exposed to environmentally realistic concentrations of used drilling muds in the sediment are unlikely to accumulate sufficient mud-associated metals to represent a toxicity hazard to themselves or to prey organisms, including Man. However, most laboratory exposures have been of short duration. It is possible that a more substantial metal bioaccumulation would be demonstrated following longer exposure periods.

RECOMMENDATIONS

The volume of research on fate and effects of drilling fluids in the marine environment, already completed or currently underway, is quite large. Perusal of this literature reveals some important gaps in our knowledge about behavior of drilling fluids discharged to the marine environment. In addition, some approaches to preventing or ameliorating drilling mud-mediated damage to the marine environment become apparent.

1. Drilling mud and solids control equipment discharge pipe design should be modified to maximize dilution of drilling mud and cuttings before they exit the pipe into the water column. A one-thousand fold dilution of drilling mud at the point of discharge should be readily obtainable.

2. The vast majority of offshore drilling muds are completely non-toxic or nearly so. An effort should be made to replace the more toxic muds and mud ingredients with less toxic ones that still will perform adequately. Mud toxicity should be included as a consideration in drilling mud program design.

3. All new drilling mud ingredients and formulations proposed for offshore use should undergo toxicological screening before permitted for offshore disposal.

4. Drilling muds used in laboratory and field biological effects studies should be characterized physically and chemically. They should be muds that have actually been used for a drilling operation. Major ingredients should be known and trace metals concentrations should be determined. The muds should be stored and used in such a way that their properties do not change.

5. Muds used for laboratory and field biological effects studies should be of types actually permitted for ocean disposal.

6. Because the major predicted impact of discharged drilling muds is on the benthos, and water column effects are expected to be minimal, regulation of drilling mud discharge rate seems inappropriate. In fact, a very high rate bulk discharge may be preferable since more of the mud will settle on the bottom in the immediate vicinity of the discharge, affecting a smaller area of bottom.

7. A flow-through exposure/bioassay system should be developed which is capable of handling complex heterogeneous mixtures like drilling muds. Mud fractions should not accumulate over time in any part of the system. Doses should be reproducible and quantifiable.

8. Long-term studies of impacts of environmentally realistic mixtures of drilling mud and sediment on benthic infauna and epifauna should be performed. These could be laboratory large-scale microcosm studies or in situ studies in and around drilling mud/cuttings piles adjacent to offshore exploratory rigs.

9. Coupled to the long-term biological effects studies, should be investigations of metal bioavailability to benthos from drilling mud-sediment mixtures. The question of the long-term bioavailability of metals to the benthos from realistic levels of drilling mud mixed with sediment is perhaps the most important single question remaining about the environmental impact of drilling muds.

10. Analytical methodology should be optimized for metals analysis in all types of drilling mud fate and effects studies. Mild digestion procedures do not adequately solubilize metals associated with barium sulfate or silicate minerals. Neutron activation is the method of choice for barium and perhaps chromium. Some effort should be made to ascertain the valency state and chemical forms of chromium in used chrome-lignosulfonate drilling muds and used chromate-treated lignosulfate muds.

11. Additional research would be useful to elucidate the mechanisms of drilling mud toxicity to very sensitive species and life stages. Is it chemical toxicity (what chemicals) or physical clogging, abrasion, or irritation of delicate gill, gut or body wall surfaces? Such information is useful for predicting the impacts of drilling fluids discharged to the ocean.

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APPENDIX I

Drilling Mud Composition

Appendix I.
Table 1a.--Drilling Mud Systems Tested under EPA, Region II Approved Joint Industry Bioassay Program.

Mud #

1. Seawater/Potassium/Polymer Mud

Components	#/BBL
KCl	5-50
Starch	2-12
Cellulose Polymer	0.25-5
XC Polymer	0.25-2
Drilled Solids	20-100
Caustic	0.5-3
Barite	0-450
Seawater	As Needed

2. Seawater/Lignosulfonate Mud

Components	#/BBL
Attapulgite or Bentonite	10-50
Lignosulfonate	2-15
Lignite	1-10
Caustic	1-5
Barite	25-450
Drilled Solids	20-100
Soda Ash/Sodium Bicarbonate	0-2
Cellulose Polymer	0.25-5
Seawater	As Needed

3. Lime Mud

Components	#/BBL
Lime	2-20
Bentonite	10-50
Lignosulfonate	2-15
Lignite	0-10
Barite	25-180
Caustic	1-5
Drilled Solids	20-100
Soda Ash/Sodium Bicarbonate	0-2
Freshwater	As Needed

Appendix I.
Table 1a. (Continued)

Mud #

4. Nondispersed Mud

Components	#/BBL
Bentonite	5-15
Acrylic Polymer	0.5-2
Barite	25-180
Drilled Solids	20-70
Freshwater	As Needed

5. Spud Mud (slugged intermittently with seawater)

Components	#/BBL
Attapulgite or Bentonite	10-50
Lime	0.5-1
Soda Ash/Sodium Bicarbonate	0-2
Caustic	0-2
Barite	0-50
Seawater	As Needed

6. Seawater/Freshwater Gel Mud

Component	#/BBL
Attapulgite or Bentonite Clay	10-50
Caustic	0.5-3
Cellulose Polymer	0-2
Drilled Solids	20-100
Barite	0-50
Soda Ash/Sodium Bicarbonate	0-2
Lime	0-2
Seawater/Freshwater	As Needed

7. Lightly Treated Lignosulfonate Freshwater/Seawater Mud

Components	#/BBL
Bentonite	10-50
Barite	0-180
Caustic	1-3
Lignosulfonate	2-6
Lignite	0-4
Cellulose Polymer	0-2
Drilled Solids	20-100
Soda Ash/Sodium Bicarbonate	0-2
Lime	0-2
Seawater to Freshwater Ratio	1:1 approx.

Appendix I.
Table 1a. (Continued)

Mud #

8. Lignosulfonate Freshwater Mud

Components	#/BBL
Bentonite	10-50
Barite	0-450
Caustic	2-5
Lignosulfonate	4-15
Lignite	2-10
Drilled Solids	20-100
Cellulose Polymer	0-2
Soda Ash/Sodium Bicarbonate	0-2
Lime	0-2
Freshwater	As Needed

Appendix I.
Table 2a. Muds Used in the Joint Bioassay Monitoring Program

MID-ATLANTIC BIOASSAY PROGRAM

*Mud Number #2 - Seawater Lignosulfonate Mud

Composition

Components	Concentration	
	#/bbl	Wt%
Barite	176.0	35.0
Bentonite/Drill Solids	32.1	6.3
Chrome Lignosulfonate	1.8**	0.4
Lignite	0.9**	0.2
Drispac (Polyanionic cellulose)	0.2	0.0
Salt	10.0	2.0
Caustic	0.9	0.2

Properties

Mud Density	12.1 lbs/gal
Percent Solids (wt%)	43.5%
Calcium	650 mg/l

Metals Analysis

Metal	Concentration (ppm-whole mud basis)
Arsenic	2.0
Barium	141,000
Cadmium	< 1
Chromium	227
Copper	11.3
Lead	< 1
Mercury	< 1
Nickel	7.5
Vanadium	18
Zinc	181

*Flowline mud samples obtained from Ocean Victory, OCS-A-0028 #3 WC; operator-Texaco. Collected March 16, 1980. Stored in refrigerator at EG&G until analysis by bioassay contractors.

**Estimated concentrations outside range for chrome-lignosulfonate (2-15 #/bbl), lignite (1-10 #/bbl).

Table 3a. Mid-Atlantic bioassay program.
*Mud Number 3 - Lime Mud

Composition

Components	Concentration	
	#/bbl	Wt%
Barite	64.0	14.7
Bentonite	20.0	5.6
Drill Solids	30.0	6.8
Chrome Lignosulfonate	3.5	0.8
Lignite	1.8	0.4
Lime	1.5**	0.5
Caustic	1.5	0.3

Properties

Mud Density	10.4 lbs/gal
Percent Solids (wt%)	27.8
pH	10.0

Metals Analysis

Metal	Concentration (ppm - whole mud basis)
Arsenic	3
Barium	76,200
Cadmium	< 1
Chromium	192
Copper	8
Lead	4
Mercury	< 1
Nickel	3
Vanadium	27
Zinc	58

*Flowline mud sample obtained from rig in Section 5 Township 10, South Range 7W, Louisiana, 3/4 miles east of Lake Charles. Collected November 1, 1980 by PESA.

**Estimated concentration outside range for lime (2-20 #/bbl)

Table 4a. Mid-Atlantic bioassay program
*Mud Number 4 - Non-Dispersed Mud

Composition

Components	Concentration	
	#/bbl	Wt%
Barite	10.8**	2.8
Bentonite	20.0**	5.2
Drill Solids	49.0	12.7
Drispac (Polyanionic cellulose)	1.0	0.3
Lignite	0.1	

Properties

Mud Density	9.2 lbs/gal
% Solids (by wt.)	21.0
Chlorides	1,200 mg/l

Metals Analysis

Metal	Concentration (ppm - whole mud basis)
Arsenic	2.0
Barium	13,300
Cadmium	< 1
Chromium	10
Copper	7
Lead	2
Mercury	< 1
Nickel	4
Vanadium	22
Zinc	16

*Flowline mud samples taken from Well No. 1, 6M&O Railroad, WC/EUCUTTA Field, Wayne County, Mississippi. Collected November 27, 1980 by PESA.

**Estimated concentration outside range for Barite (25-180) and Bentonite (5-15).

Table 5a. Mid-Atlantic bioassay program
*Mud Number 5 - Seawater Spud Mud

Composition

Components	Concentration	
	#/bbl	Wt%
Barite	2	.5
Drill Solids	52	15.0
Bentonite	22	6.3
Lime	0	0
Soda Ash/Sodium Bicarbonate	0	0
Caustic	0	0

Properties

Mud Density	8.2
Percent Solids (by wt)	21.7

Metals Analysis

Metal	Concentration (ppm - whole mud basis)
Arsenic	3
Barium	2,800
Cadmium	<1
Chromium	16
Copper	5
Lead	4
Mercury	<1
Nickel	6
Vanadium	35
Zinc	21

*Flowline mud samples obtained Ship Shoal, Block 224, OCS6-10-23, Well D7, Nobel-27. Collected October 23, 1980 by PESA.

Table 6a. Mid-Atlantic Bioassay program
*Mud Number 6 - Seawater/Freshwater
Gel Mud

Composition

Components	Concentration	
	#/bbl	Wt%
Barite	21.2	5.4
Bentonite	9.7**	2.5
Drill Solids	14.1**	3.6
Drispac (Polyanionic cellulose)	0.5	0.1
Cellex (CMC)	0.1	0.0
Caustic	0.4**	0.1

Properties

Mud Density	9.3 lbs/gal
% Solids (by wt)	11.6
Chlorides	250 mg/l
Calcium	40 mg/l

Metals Analysis

Metal	Concentration (ppm - whole mud basis)
Arsenic	2
Barium	25,600
Cadmium	< 1
Chromium	2
Copper	2
Lead	< 1
Mercury	< 1
Nickel	1
Vanadium	6
Zinc	12

*Flowline mud samples taken from rig in Standard Draw Z-10, Carbon County, Wyoming. Collected November 1, 1980 by PESA.

**Estimated concentration outside range for Bentonite (10-50), Drill Solids (20-100), Caustic (0.5-3).

Table 7a. Mid-Atlantic bioassay program
*Mud Number 7 - Lightly Treated
Lignosulfonate Freshwater/Seawater
Mud

Composition

Components	Concentration	
	#/bbl	wt %
Drill Solids	48	12
Bentonite	25	6.2
Barite	9	2.2
Chrome Lignosulfonate	4	1.0
Lignite	5	1.2
Cellulose Polymer (Drispac)	0.5	0.1

Properties

Percent Solids (wt%)	24.1%
Mud Density	9.6 lbs/gal
pH	10.8
Chlorides	7500 mg/l

Metals Analysis

Metal	Concentration (ppm-whole mud basis)
Arsenic	<1
Barium	11,500
Cadmium	<1
Chromium	265
Copper	26
Lead	24
Mercury	<1
Nickel	6
Vanadium	30
Zinc	82

*Flowline mud sample obtained from Alaskan Star Drilling for Exxon USA in Block 599 Exxon OCS A-0029 Well #1.

Table 8a. Mid-Atlantic Monitoring Program
*Mud Number 8 - Lignosulfonate
Freshwater Mud

Composition

Components	Concentration	
	#/bbl	Wt%
Barite	15.1	3.9
Bentonite	15.1	3.9
Drill Solids	28.1	7.2
Chrome Lignosulfonate	1.7**	0.4
Lignite	2.8	0.7
Caustic	1.2**	0.3
Lime	Trace	-

Properties

Mud Density	9.3 lbs/gal
% Solids (by wt)	16.4
Chlorides	1800 mg/l
pH	9.0
Calcium	40 mg/l

Metals Analysis

Metal	Concentration (ppm - whole mud basis)
Arsenic	3
Barium	14,000
Cadmium	< 1
Chromium	48
Copper	4
Lead	9
Mercury	< 1
Nickel	8
Vanadium	18
Zinc	15

*Flowline mud sample obtained from South Allenhorst Prospect, Caney Field, C. R. Bostwick and Brotherton Survey A-6, Matagora County, Texas. Collected November 16, 1980 by PESA.

**Estimated concentrations outside range for Chrome-Lignosulfonate (4-15), Caustic (2-5).

Appendix
Table 9a. Range of chemical and physical characteristics for the various types of drilling fluids and seawater used in bioassays. Most metal concentrations were determined by Flame AAS techniques. Barium was determined by graphite furnace AAS. Cadmium in seawater was determined by ASV techniques. Detection limits for trace metals are also indicated (From Tornberg et al., 1980).

Drilling Fluid Type	Depth of Well (m)	Density (kg/l	pH	mg/l						
				Ba	Cd	Cr	Cu	Pb	Hg	Zn
a. drilling fluids										
CMC/Gel (2 samples)	1807-2653	1.21-1.23	10.0-10.5	4400-6240	≤0.5-0.6	28-63	6.4-10.4	2.4-12.8	0.017-0.031	42-64
XC-Polymer (20 samples)	2784-3645	1.14-1.23	9.0-12.1	720-1170	≤0.5-1.5	66-176	10.0-16.0	5.6-56.0	0.015-0.070	49-110
XC-Polymer/ Unical (6 samples)	3139-4175	1.21-1.32	10.0-11.0	N.A.	N.A.	56-125	2.8-17.0	9-117	0.028-0.217	198-397
Lignosulfonate Drilling Fluid (4 samples)	2256-2692	1.15-1.23	10.0-11.0	800-7640	≤0.5	121-172	10.0-12.0	16.4-56.0	0.03-0.07	49-56
Detection Limit				0.10	0.5	2.0	2.0	2.0	0.010	2.0
b. ambient seawater										
Ambient Seawater (23 samples)*			7.9-8.4	≤0.02-0.04	≤.005-.019	≤0.025	0.01-0.047	≤0.001	≤0.0002	≤0.010-0.068
Detection Limit				0.02	0.005	0.025	0.001	0.001	0.0002	0.010

N.A. not available
* n=3 samples for barium

APPENDIX II

Ongoing Research Programs on Effects of Used Drilling Muds on Marine Animals

APPENDIX II. Ongoing research programs on effects of used drilling fluids and drilling fluid ingredients on marine organisms and ecosystems. Included are investigations that were completed within the last year and for which a final report was not available to J.M. Neff. This list is not comprehensive.

1. PI, Richard E. Dodge, Nova University. Sponsor, EPA. "Effects of Drill Mud Effluent on Coral Growth: *Montastrea annularis*".

   Corals were stained with Alizarin Red S and exposed for 50 days to nominal 0, 1, 10, and 100 ppm drilling mud effluent. Drilling mud type, source and exposure scheme were not described. Upward growth of coral skeleton was depressed by long-term exposure to 100 ppm drilling mud effluent. At this concentration, 2 out of 3 colonies died by 50 days. Other concentrations of drilling mud were without effect on coral growth and survival. Changes in coralite shape were variable at different exposure concentrations. There was considerable variability in growth parameters of both control and drilling mud-exposed corals.

2. PI, A. Szmant Froelich, Florida State University. Sponsor, EPA. "Effects of Oil Drilling Muds on the Physiology and Nutritional Status of *Montastrea annularis*".

   Corals were exposed for six weeks to nominal 0, 1, 10 and 100 ppm drilling mud. Drilling mud type, source and exposure scheme were not described. At an exposure concentration of 100 ppm, respiration of corals was decreased by approximately one-half and calcification rate was decreased to one-tenth that of controls. Several corals exposed to 100 ppm drilling mud died. Abundance of symbiotic zooxanthellae in tissues of corals exposed to 100 ppm drilling mud was significantly lower than in controls, resulting in lower nitrogen fixation and gross photosynthesis rates in mud-exposed colonies. Lower drilling mud concentrations were without significant effect.

3. PI, James W. Porter, University of Georgia. Sponsor, EPA. "Effects of Drilling Fluids on Coral Respiration, *Montastrea annularis*".

   Reports not available.

4. PI, Gerald Schatten, Florida State University. Sponsor, not known. "Effects of Barium on Fertilization and Early Development in Sea Urchin Embryos".

   Barium sulfate in normal seawater and barium chloride in sulfate-free seawater prevented normal fertilization and induced polyspermy in eggs of the sea urchin *Lytechinus variegatus*. The author hypothesized that trace barium ion interferes with calcium uptake by sperm during the acrosome reaction, allowing polyspermy to occur. Barium ion concentrations required to elicit this response were not measured.

5. PI, Richard B. Crawford, Trinity College. Sponsor, EPA. "Effects of Used Drilling Muds on Development of *Fundulus heteroclitus, Echinarachius parma* and *Lytechinus variegatus*".

Embryos were exposed to nominal concentrations of 1, 10, 100, and 1000 ppm used drilling muds from Mobile Bay, AL. Muds were collected on March 12, April 24, May 29, June 26 and October 11, 1979. Results of experiments with fish and sand dollar embryos were discussed in the main body of this review, based on the publication of Crawford and Gates (1981). Eggs of the sea urchin *Lytechinus variegatus* behaved similarly to eggs of sand dollars. At a nominal 1000 ppm drilling mud, development was arrested at the blastula stage. The October mud was the most toxic and the March mud the least toxic. If unfertilized eggs were exposed to 10,000 ppm used drilling mud, subsequent fertilization was inhibited.

In experiments with *Fundulus* embryos, 1000 ppm of the June 26 and October 11 muds reduced hatching. The March 12 mud produced the same effect at 10,000 ppm. The April 24 and May 29 muds were not toxic at any concentration tested.

6. PI, Paul V. Hamilton, University of West Florida. Sponsor, EPA. "Effects of Drilling Muds on Shell Movement in *Argopecten irradians*".

Scallops were exposed to barite (IMCO-BAR), chromate-treated chrome lignosulfonate (IMCO RD-111), calcium carbonate or used Mobile Bay drilling mud obtained August 7, 1979. Of five valve movement parameters measured electronically, only two were considered reliable indicators of response (change in number of major valve closures and change in cumulative valve closure magnitude). Whole drilling mud significantly increased the number of major valve closures at concentrations above 400 ppm and significantly increased the cumulative magnitude of valve closures above 200 ppm. Responses to barite, lignosulfonate and calcium carbonate were similar to one-another but different from responses to whole used mud. Maximal response to the pure particulate compounds was observed at 200 ppm. Higher doses resulted in lesser responses. The investigators suggested that behavioral responses observed represented increased pseudofecal production by the scallops to cleanse gills of accumulated foreign particles.

7. PI, Jelle Atema, Boston University, Sponsor, EPA. "Effects of Used Drilling Muds on Lobsters *Homarus americanus*".

Some of the results from this program were discussed above (Derby and Atema, 1981). Effects of exposure for 30 days in a flow-through system to a nominal 10 ppm used drilling mud (designated J-5) or a natural marine mud on stage IV postlarvae of lobsters was studied. Exposure to drilling mud had no effect on survival but did result in increased loss of appendages, apparently through difficulty in molting. The molt from stage IV to stage V was not influenced by treatment but the subsequent molt from stage V to VI was. There was a significant disruption and delay in molting among drilling mud exposed animals. There was little or no effect of drilling mud on feeding rate or feeding responses.

Burrowing responses of lobsters to three muds (J5, J7 and Mobile 16) were measured. Lobsters preferred natural mud to sediment with a 1-mm layer of J7 or Mobile 16 mud. J5 mud was without effect. A 1-mm layer of drilling mud caused a delay in burrow construction and caused lobsters to leave prexisting burrows. A 4-mm layer of Mobile 25 drilling mud seriously interferred with burrow construction. A 4-mm layer of a barite/bentonite mixture had the same effect on burrow construction as drilling mud.

Effect of exposure for up to four months in a flow-through system to 10 ppm of three used Mobile Bay drilling muds (collected May 29, June 26, and September 4, 1979) on survival and behavior of juvenile lobsters was investigated. The drilling mud from June 26 was without effect on the juvenile lobsters. Lobsters exposed to the other two muds showed a substantial loss of feeding behavior, both in slower alerting to the presence of food and in a longer search time before finding food. These two drilling mud samples produced 100% mortality in 15 days at a nominal 10 ppm drilling mud. Whether mud components accumulated over time in the exposure system was not discussed.

When lobsters were given a choice between clean natural mud substrate and substrate overlain with 1-2 mm Mobile Bay used drilling mud, they always chose the drilling mud-free substrate. When a layer of used drilling mud was introduced to the "clean" side of the aquaria, the lobsters left their burrow.

8. PI, Thomas R. Gilbert, New England Aquarium. Sponsor, EPA. "Impact of Discharged Drilling Fluids on the Georges Bank Environment".

This is a multi-faceted investigation involving chemical characterization of drilling muds used by several EPA drilling mud program investigators, bioassay and sublethal effects studies with several species of marine animals, and recruitment/recolonization studies. Several drilling mud samples including Mobile Bay muds, "Jay muds", and API muds were analyzed for physical and chemical characteristics, trace element composition, and organic constituents. There were no consistent correlations between concentration of inorganic components of muds and their toxicities. In some but not all cases, muds high in dissolved chromium were more toxic than muds containing low dissolved chromium concentrations. Several muds contained diesel oil, and these were generally more toxic than those which did not contain oil.

Bioassays were performed with several used drilling muds and the copepods *Acartia tonsa* and *Centropages typicus*. Three drilling muds collected from Mobile Bay on May 15, May 29 and September 4 had acute toxicities to *Acartia tonsa* of 0.026, 0.091 and 0.61 ml mud/liter, respectively (equivalent to 26, 91 and 610 ppm mud added). If the preparations were allowed to settle for one hour to three days before the bioassay, toxicity decreased substantially to more than 1,000 ppm in all cases. Toxicity of the two May muds appeared to be due primarily to settleable particles, while that of the September mud was due primarily to soluble materials. Five used muds from other sources had acute toxicities ranging from 2.4 to >10 ml mud/liter (2,400->10,000 ppm). *Centropages typicus* was about as sensitive as *Acartia* to used drilling muds. Exposure concentrations only slightly lower than acutely toxic concentrations were required to significantly reduce fecundity in *Acartia tonsa*. Juveniles were no more sensitive to used drilling muds than adults.

Exposure for 96 hours of larvae of the ocean scallop *Placopecten magellanicus* to 1-ml/liter (1,000 ppm) May 15 Mobile Bay drilling mud, 0.3 ml/ℓ (300 ppm) May 29 mud, or 0.1 ml/ℓ (100 ppm) September 4 mud significantly inhibited shell formation. If surviving larvae were returned to clean seawater after exposure, they were unable to recover from arrested shell development. Drilling muds from other sources were less toxic than the September 4 Mobile Bay mud to scallop larvae.

Larvae of the crab *Cancer irroratus* were much more tolerant than scallop larvae to the September 4 drilling mud sample. Exposure to concentrations up to 100 µℓ/ℓ (100 ppm) had no effect on larvae survival or molting. Stage III larvae exposed to 100 ppm drilling mud initially consumed *Artemia* nauplii at a higher rate than controls did. After 96 hours, mud-exposed larvae had a lower consumption rate than controls. If allowed to recover in clean seawater, mud exposed larvae resumed normal feeding. The 96-hr LC50 of the liquid phase of used September 4 drilling mud to 5-day-old *Cancer* larvae was 1.02 ml mud/liter (1,020 ppm mud added), similar to the LC50 of this mud to *Acartia*.

Juvenile winter flounder *Pseudopleuronectes americanus* were unaffected by exposure to 8.7 ml/ℓ (8,700 ppm) of May 29 drilling mud. Seventy-day-old postmetamorphosis winter flounder were unaffected by exposure for 48 hours to 1 ml/liter (1,000 ppm) of five drilling muds. Exposure of unfertilized eggs of flounder to drilling mud had no effect on subsequent fertilization and embryonic development in clean seawater.

Flounder larvae were exposed for 48 hours to 1 ml/liter suspensions of five used drilling muds. Larvae seemed to exhibit avoidance behavior when exposed initially to drilling mud suspensions. Some larvae exposed to two Mobile Bay muds died. When returned to clean seawater, all surviving larvae continued to survive and appeared normal.

Recruitment/recolonization studies were performed using several grain sizes of natural sediment, ground silica and drilling muds. Deposition of detritus from the flowing seawater was uneven in the circular tanks and affected recruitment of planktonic larvae to the different substrates. There was a tendency for control substrates to support larger populations than mud-treated substrates. The system is being redesigned to provide more uniform water flow. Field recruitment studies are also underway.

9. USN/NOAA. Sponsor, EPA. "Environmental Effects of Offshore Drilling and Oil on the Marine Environment".

10. Yale University. Sponsor, EPA. "The Erodibility of Drilling Muds Deposited on the Sea Floor".